Über die unregelmässige Reihe der kolloiden Lösungen durch Elektrolyten. VI. Die vergleichenden Versuche der Koagulationskurven verschiedener Sulfidsole.[1]

Von Naoyasu SATA und Sigeru ITÔ.

(Eingegangen am 20. April 1942.)

(1) Einleitung. Wir haben schon die unregelmässige Reihe des HgS-Sols von recht mannigfaltigen Seiten untersucht. Dadurch erklärt sich, dass diese Erscheinung an allen untersuchten HgS-Solen ohne Ausnahme nachweisbar ist, d.h. die Ausgangsmaterialien, beigemischte Fremdionen, die Beständigkeit, die Reinheit usw. des Sols haben mit der unregelmässigen Reihe nicht viel zu tun.

Nun haben wir infolgedessen noch eine Frage aufgeworfen, ob sie eine spezielle Eigenschaft des HgS-Sols ist oder bei allen mit H_2S stabilisierten Sulfidsolen eine allgemein erkennbare Erscheinung ist, welche sich durch genau gleiche Methode herstellen lässt. Es ist nämlich die Herstellungsmethode von HgS-Sol nach Winssinger prinzipiell an allen Sulfidsolen anwendbar, wenn man ein geeignetes Salz als Ausgangsmaterial findet. Daraus können wir vielleicht annehmen, dass die Oberflächenstruktur oder der Stabilisierungsmechanismus der Teilchen der nach gleicher Winssinger-Methode hergestellten Sulfidsole voneinander sehr ähnlich sein möge. Somit wäre das Adsorptionsverhalten des $AgNO_3$ auf diesen *strukturell* verwandten Sulfidsolen auch wahrscheinlich ähnlich, da die Adsorption eine Oberflächenerscheinung ist. Schliesslich wurde konstatiert, dass die nach Winssinger-Methode hergestellten verschiedenen Sulfidsolen allgemein die unregelmässige Reihe zeigen. Von diesen Gesichtspunkten aus haben wir nachstehend zuerst die Anwendbarkeit der Winssinger-Methode an verschiedenen Sulfidsol-Darstellungen untersucht und dann das Vorhandensein der unregelmässigen Erscheinung bei der Koagulation so hergestellter Solen geprüft.

(2) Die Herstellung verschiedener Sulfidsole. Von der Verwandtschaft mit Quecksilber haben wir zuerst als Sulfid-Material Cadmium und Zink ausgewählt.

Herstellungsvorschriften und Sol-Eigenschaften sind folgende.

(i) *CdS-Sol.* CdS-Sol nach Winssinger-Methode wurde schon von E. Prost[2] untersucht. Er hat das Sulfid aus $CdSO_4$-Lösung unter Zusatz von Ammoniak gefällt, was vielleicht zu vollkommenem Niederschlagen der Cd-Ionen geführt hat und wovon die Sol-Beständigkeit in gewissem Sinne abhängig gemacht wird. Wir haben den Versuch unter verschiedenen Bedingungen ausgeführt.

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(1) N. Sata u. Y. Niwase, *Kolloid-Z.*, **84** (1938), 314; N. Sata u. S. Itô, dieses Bulletin, **15** (1940), 271; N. Sata u. K. Môri, ebendort, **16** (1941), 139; N. Sata u. S. Itô, ebendort, **17** (1942), 4.

(2) The Svedberg: Herstellung kolloider Lösungen anorganischer Stoffe. (Dresden und Leipzig, 1922) S. 391, 404.

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(a) Von 100 ccm. 2.5% $CdSO_4$-Lösung wurde das CdS mit H_2S gefällt unter Zusatz von 15 ccm. 6N-NH_4OH. Den Niederschlag wäscht man durch Dekantieren (3-mal). Die Suspension wurde peptisiert mit abermaligem H_2S-Durchleiten. Überschüssiger H_2S wurde mit H_2 ausgetrieben. Beständigkeit ist gut. Der Koagulationswert mit $NaCl=50$; $CaCl_2=0.6$; $AlCl_3=0.8$ Millimol./Lit.

(b) Das CdS-Sol wurde hergestellt wie oben, aber ohne NH_4OH-Zusatz. Der Niederschlag liess sich nicht vollkommen peptisieren und lässt etwas Bodensatz zurück. Die Beständigkeit ist nicht so gut wie beim vorigen Fall, so z.B. setzt sich der Ko. W. (Abkürzung für Koagulationswert.) mit NaCl zu 2 Millimol./Lit. herab.

(c) Das CdS-Sol (i), (a) wurde dialysiert für 11 Tage (nach 4 Tagen ist es koaguliert) und dann wieder mit H_2S peptisiert. Es ist doch viel beständiger als das CdS-Sol (i), (b), welches ohne Ammoniak hergestellt ist.

(ii) *ZnS-Sol.* Das Sol ist auch von C. Winssinger[3] hergestellt. Verschiedene Herstellungsmöglichkeiten haben wir untersucht. In diesem Fall ist NH_4OH unentbehrlich zum Peptisieren; d.h. aus $ZnSO_4$ unmittelbar gefälltes Sulfid lässt sich nicht mit H_2S peptisieren. Sondern man musste zuerst mit NH_4OH gefälltes Zn-Hydroxyd durch H_2S-Leiten in Sulfid umwandeln und gleichzeitig kolloidal peptisieren lassen.

(a) Einer 100 ccm. 2.5% $ZnSO_4$-Lösung wurde 6 ccm. 6N-NH_4OH zugesetzt. Ausscheidung von weissem, flockigem Zn-Hydroxyd-Niederschlag. Man leitet H_2S durch diese Hydroxyd-Suspension, um sie zur Sulfid-Suspension zu verwandeln. Da diese Suspension schwer absetzbar ist, musste man sie vor der Reinigung durch Dekantieren zentrifugieren, was nur 2-mal zu gestatten war. Vor dem dritten Dekantieren ist die Suspension automatisch peptisiert, ohne abermaliges H_2S-Durchleiten vollkommen, nur durch Umrühren eines Glasstäbchens. Noch übriggebliebenes H_2S wurde mit Durchleiten von H_2 ausgetrieben.

(b) Das ZnS-Sol (ii), (a) kann man durch Erhitzen (98°C) koagulieren. Nach dem Dekantieren, peptisiert der grösste Teil des Niederschlags sich wieder durch einfaches Umrühren mit von neuem zugefügten Wasser. Diese Behandlung—Koagulieren durch Erhitzen, Zentrifugieren, Dekantieren und Peptisieren—wiederholt man 8-mal. Durch die Suspension wurde zuletzt zum vollständigen Peptisieren H_2S durchgeleitet.

(c) Das ZnS-Sol (ii), (a) wird dialysiert für 7 Tage. (Nach 3 Tagen ist es koaguliert.) Danach wurde die Suspension wiederum mit H_2S peptisiert. In der Lösung NH_4- und SO_4-Ionen nicht nachweisbar. Tabelle 1 ergibt die Koagulationswerte dieser Sole in Millimol./Lit.

Tabelle 1.

Elektrolyt	NaCl	$CaCl_2$	$AlCl_3$
(ii), (a) 2-mal dekantiert	20	0.4	0.3
(ii), (b) 8-mal dekantiert mit Wärmeanwendung.	10	0.2	0.1

(3) *loc. cit.* (2), S. 299.

(iii) *As_2S_3-Sol.* Zur Kontrolle haben wir auch As_2S_3-Sol als einen Versuchsgegenstand ausgewählt. Bei diesem Sol ist besonders darauf zu achten, dass bei ihm ausser stabillisierenden H_2S keine beigemischten Fremdsubstanzen zu ahnen sind, wie die Reaktionsformel es zeigt:

$$As_2O_3 + 3H_2S \rightarrow As_2S_3 + 3H_2O$$

(3) **Die Koagulationsversuche.** Die Koagulationsversuche, mit $AgNO_3$ als Elektrolyt, wurden dann an oben erhaltenen verschiedenen Sulfidsolen ausgeführt. Wie schon erwähnt, ist der Koagulationsversuch dieser Art ein sehr heikles Experiment. So haben wir diesmal die Koagulation nicht nur durch Trübung oder Flockenbildung entschieden, sondern

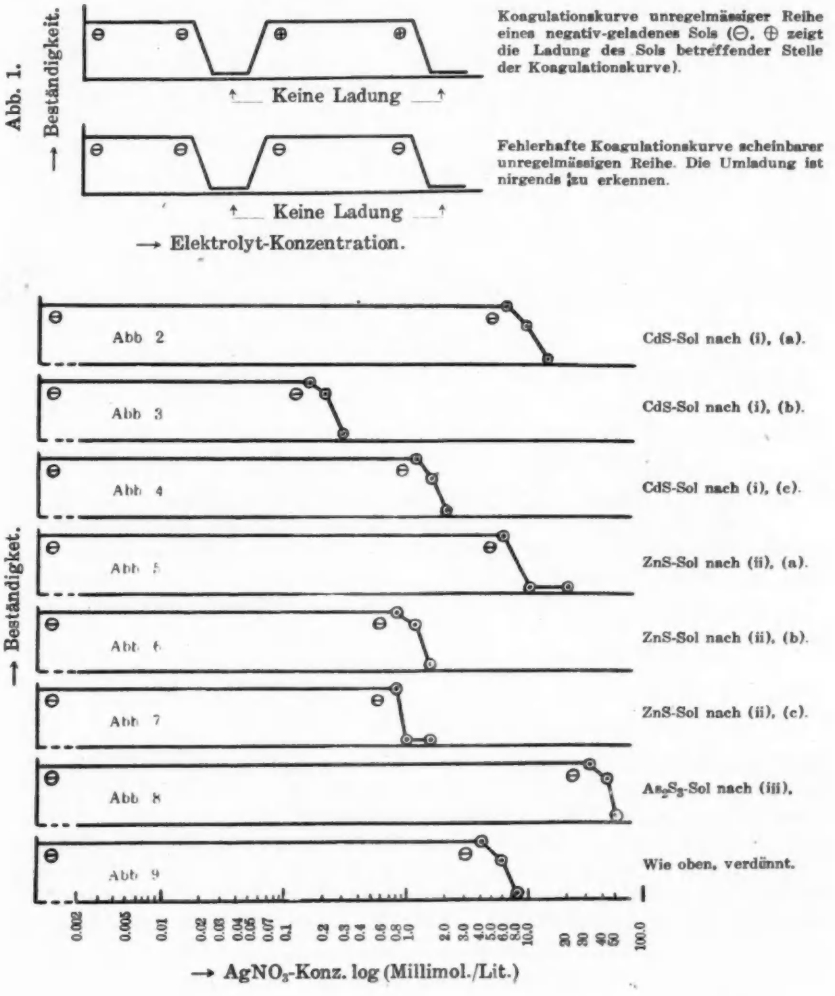
Abb. 1.
Beständigkeit.
Keine Ladung
Keine Ladung
Elektrolyt-Konzentration.
Koagulationskurve unregelmässiger Reihe eines negativ-geladenes Sols (⊖, ⊕ zeigt die Ladung des Sols betreffender Stelle der Koagulationskurve).
Fehlerhafte Koagulationskurve scheinbarer unregelmässigen Reihe. Die Umladung ist nirgends zu erkennen.
Abb 2
Abb 3
Abb 4
Abb 5
Abb 6
Abb 7
Abb 8
Abb 9
CdS-Sol nach (i), (a).
CdS-Sol nach (i), (b).
CdS-Sol nach (i), (c).
ZnS-Sol nach (ii), (a).
ZnS-Sol nach (ii), (b).
ZnS-Sol nach (ii), (c).
As2S3-Sol nach (iii).
Wie oben, verdünnt.
Beständigkeit.
0.002 0.005 0.01 0.02 0.03 0.04 0.05 0.07 0.1 0.2 0.3 0.4 0.5 0.8 1.0 2.0 3.0 4.0 5.0 6.0 8.0 10.0 20 30 40 50 100.0
AgNO3-Konz. log (Millimol./Lit.)

noch dazu durch Elektrophorese die Teilchenladung nachgesehen. Auf diese Weise kann man die Koagulationskurve vor einem Versuchsfehler garantieren. Bei dem Koagulationsversuche kommt manchmal eine fehlerhafte Koagulation vor, welche durch unerwartete Verunreinigungen in Versuchsgefässen usw. ganz zufälligerweise hervorgerufen wird. In diesem Fall könnte die Koagulationskurve wie eine unregelmässige Reihe verlaufen, doch in Wirklichkeit ist gar keine, zur unregelmässigen Reihe charakteristische Umladung zu erkennen, was nur durch kataphoretische Untersuchung zu unterscheiden ist. Abb. 1 macht den Vorgang schematisch ersichtlich. Abb. 2–9 sind die Koagulationskurven der verschiedenen Sulfidsole.

(4) **Erörterung.** Das sogenannte nach „Winssinger Methode" bekannte Herstellungsverfahren des HgS-Sols ist prinzipiell bei verschiedenen Sulfidsolen allgemein anwendbar. Da in diesem Fall der H_2S zum Stabilisieren die Hauptrolle zu spielen hat, könnte man für alle Teilchen dieser Sulfidsole ganz gleiche oder wenigstens sehr ähnliche Oberflächenstruktur annehmen, wie aus Abb. 10 zu ersehen ist.[4] Unter weiteren Annahme, dass solche ähnlich konstruierten Teilchen mit gleichem Elektrolyt ($AgNO_3$) auch gleicherweise die unregelmässige Koagulation wie HgS-Sol zeigen würde, haben wir obenstehende Untersuchung angestellt. Wie die Versuchsresultate aus den Abb. 2–9 erkennen lassen, erweist sich diese Vermutung als völlig haltlos, denn keins von den untersuchten Sulfidsolen zeigt die unregelmässige Reihe. Daraus wird konstatiert, entweder die Oberflächenstruktur der Teilchen verschiedener Sulfidsole

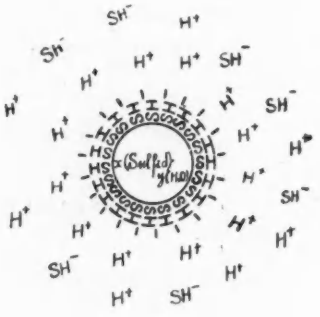

Abb. 10.

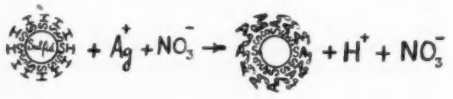

Abb. 11.

nicht ganz ähnlich anzunehmen ist, oder das HgS-Sol allein besitzt eine eigenartige Adsorptionseigenschaft mit $AgNO_3$ die unregelmässige Koagulation hervorzurufen. Wir haben schon bestätigt, dass die unregelmässige Reihe des HgS-Sols von beigemischten Fremdionen, die von verschiedenen Ausgangsmaterialien stammen, nicht beeinflusst wird. Noch dazu, weil der HgS-Niederschlag vor dem Peptisieren durch Dekantieren genügend gereinigt ist, könnte man leicht auf den Gedanken kommen, dass die

(4) H. B. Weiser, "Inorganic Colloid Chemistry," Vol. III, S. 212.

übriggebliebenen Fremdionen nach dem Peptisieren hauptsächlich auf der Teichenoberfläche oder in ihrer diffusen Schicht verteilt worden sind. Dass diese Fremdionen auf der Teilchenoberfläche zur Entstehung der unregelmässigen Reihe nichts zu tun haben, legt uns die Vermutung nahe, dass die Ursache in der Verbindungsart von $AgNO_3$ an HgS-Oberfläche zu suchen ist. Ausserdem bei der Ausführung der Koagulationsversuche, konnten wir nachweisen, dass das anfangs neutrale HgS-Sol nach dem Zusatz der auch neutralen $AgNO_3$-Lösung sauer geworden ist, woraus man die Wahrnehmung machen kann, dass hier eine polare Adsorption stattgefunden hat. Mitunter verstehen wir, dass zwischen SH-Ionen auf der Teilchenoberfläche und Ag-Ionen eine Austauschadsorption geschieht, wie aus Abb. 11 schematisch ersichtlich ist.

Wir kommen somit zum Schluss, dass eine weitere Überlegungsmöglichkeit hinsichtlich der Spezifität der unregelmässigen Reihe von HgS-Sol noch von der Seite des Adsorptionsproblems her zu finden ist. Die endgültige Diskutierung ist aus den Resultaten vergleichender Adsorptionsversuche von $AgNO_3$ an verschiedenen Sulfiden zu erwarten, welche schon im Gang ist.

Zusammenfassung.

(1) Um die Entstehung der unregelmässigen Reihe bei verschiedenen Sulfidsolen zu prüfen, wurde zuerst die Anwendbarkeit der sogenannten „Winssinger Methode" zur Herstellung verschiedenen Sulfidsolen untersucht.

(2) Das Sulfidsol von Zn, Cd und As wurde nach dieser Methode unter variirenden Bedingungen hergestellt und ihre kolloidwissenschaftlichen Eigenschaften untereinander verglichen.

(3) Es wurden die Koagulationsversuche, mit $AgNO_3$ als Elektrolyt, an so erhaltenen, verschiedenen Sulfidsolen angestellt.

(4) Die unregelmässige Koagulationsreihe liess sich bei keinem Sulfidsol, ausser HgS-Sol, nachweisen.

(5) Dadurch wurde konstatiert, dass die unregelmässige Reihe auf eine spezielle Adsorptionseigenschaft von Ag- bzw. NO_3-Ionen an HgS-Teilchen zurückzuführen ist.

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Geochemische Untersuchungen der Vulkane in Japan. XXVI. Dichtemessungen des Flusswassers. I.

Von Shinya OANA.

(Eingegangen am 21. Mai 1942.)

Einleitung. Es ist heutzutage äusserst schwierig, in irgend einem natürlichen Wasser die Mengenverhältnisse der schweren Sauerstoff- und Wasserstoffisotopen durch direkte Methoden genau zu ermitteln, obwohl gerade diese Frage im Gebiete der Geochemie von hohem Interesse ist. Man muss sich in der Gegenwart damit begnügen, dass man den Unterschied der summierten Konzentrationen der schweren Wasserisotopen in zwei verschiedenen Proben aus natürlichen Gewässern bestimmen kann. Die Dichte des Wassers steigt in dem Masse, in dem sich die Konzentrationen der schweren Wasserisotopen vergrössern. Wenn wir den Dichteunterschied zweier Proben vollständig gereinigten Wassers bis zu einer Genauigkeit von 0.1 γ bestimmen (0.1 γ ist die bis heute erreichte kleinste Fehlergrenze bei diesen Arbeiten), so können wir damit einen geringsten Unterschied der summierten Konzntrationen der schweren Wasserisotopen von 0.00009% der Atomanzahl erfassen. Es ergibt sich die Notwendigkeit, den Untersuchungen hinsichtlich der Dichte unveränderliches Wasser als Standard-Wasser zu Grunde zu legen. Wegen der Bequemlichkeit der Beschaffung habe ich das Leitungswasser der Stadt Tokio seit dem Anfang meiner Arbeit über Wasserisotopen als Standard gewählt. Etwa einmal im Jahre wird das Standard-Leitungswasser in grosser Menge bereitet. Zwischen den bis heute hergestellten Portionen des Standard-Leitungswassers konnte ich keinen Dichteunterschied beobachten. Worauf beruht diese Unveränderlichkeit der Dichte?

Um dieses Problem zu lösen, habe ich den Fluss Tamagawa entlang, der mein Standard-Leitungswasser liefert, eine Reihe von Wasserproben gesammelt und durch Schwimmermethode ihre Dichte bestimmt. Diese, die an dem Oberlauf sehr klein ist, wird im weiteren Laufe des Tamagawa-Flusses grösser, um schliesslich von einem gewissen Ort des Unterlaufs an den Wert 0 γ zu erreichen und unveränderlich beizubehalten.

Ich habe auch bei anderen Flüssen entsprechende Verhältnisse beobachtet. Über diese Erscheinung wird weiter unten näherer berichtet.

Methoden der Versuche. Die Reinigungsprozesse des Wassers und die Methoden der Dichteunterschiedsbestimmung zwischen natürlichen Wässern und dem Leitungswasser der Stadt Tokio wurden in früheren Mitteilungen[1] beschrieben.

Ergebnisse der Versuche. Bis heute liegen vier Portionen des Standard-Leitungswassers vor, das jedesmal in einer Menge von etwa 20 l. in einer Glasflasche aufbewahrt wird und bei den Dichtemessungen eines natürlichen Wassers als Standard dient. Die Dichteunterschiedsbestim-

(1) S. Oana, Dieses Bulletin, **14** (1939), 279.

mungen zwischen den früheren drei Standards und dem letzten sind in Tabelle 1 wiedergegeben.

Tabelle 1. Dichteunterschiede zwischen verschiedenen Portionen des Standard-Leitungswassers.

Datum	Dichteunterschied, γ
15. Apr. 1936.....	0.0_0
10. Nov. 1938.....	-0.0_9
13. Mai 1940.....	$+0.0_4$
31. Jan. 1941.....	Standard

Aus dem Tamagawa-Fluss, der obengenannte Standards geliefert hat, wurden an verschiedenen Stellen seines Laufs 9 Wasserproben entnommen und geprüft. Die gewonnenen Resultate enthält Tabelle 2.

Die genannten Orte sind in Abb. 1 eingezeichnet.

Ein gleicher Versuch wurde bei einem anderen Flusse, dem Adusagawa durchgeführt. Die gewonnenen Ergebnisse sind in Tabelle 3 enthalten.

Tabelle 2. Dichteunterschied zwischen dem Flusswasser von Tamagawa und dem Standard-Leitungswasser.

		Entfernung vom Ursprung, km.	Tageszeit, am 22. Sept. 1941	Luft-temperatur, °C.	Fluss-temperatur, °C.	*p*H	Dichte-unterschied, γ
1	Taba	17.....	17h (am 21.)	16.2	13.1	7.0	-1.0_5
2	Yuba	31.....	5h 40	11.2	13.0	7.4	-1.3_2
3	Bentenkio	41.....	7h 5	12.3	13.4	7.1	-0.5_3
4	Nipparagawa bei Hikawa	(17)....	7h 40	13.0	12.6	7.7	-0.7_0
5	Hikawa	41.5 ...	8h 10	15.2	13.0	7.5	-0.8_3
6	Mitake	53.....	9h 20	16.0	14.2	8.1	0.0_0
7	Hamura	70.....	12h 10	21.5	16.1	7.4	-0.1_8
8	Oberes Sammelbecken des Leitungswassers bei Murayama		14h 50	22.0	20.0	7.5	-0.1_3
9	Unteres Sammelbecken.		15h 0	21.2	21.2	7.4	-0.0_4

4. Nipparagawa ist ein Nebenfluss, der bei Hikawa in den Tamagawa einmündet, und die Laufstrecke des ersteren bis hierher beträgt 17 km.

7, 8, 9. Das Leitungswasser wird von Hamura bis zum oberen Sammelbecken bei Murayama durch eine Röhre aus Zement geleitet und dann aus dem unteren Becken der Stadt Tokio geliefert, nachdem es bereits im oberen von suspendierten Stoffen befreit wurde.

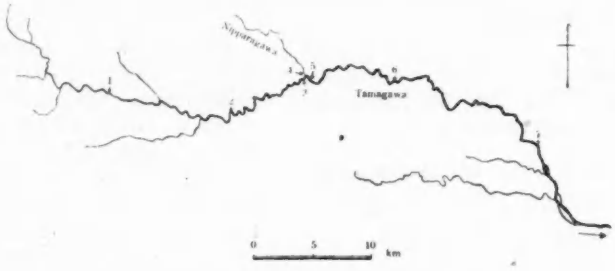

Abb. 1. Tamagawa-Fluss.

Tabelle 3. Dichteunterschied zwischen dem Flusswasser von Adusagawa und dem Standard-Leitungswasser.

	Herkunft der Wasserprobe	Entfernung vom Ursprung, km
10	Schneereste vom Karasawa-Firn	(0)
11	Bächlein bei der Berghütte Karasawagoya	(0)
12	Nebenfluss Karasawa bei der Brücke Hondanibasi	(1.5)
13	Nebenfluss Karasawa bei der Felsengrotte von Yokoo	(4)
14	Adusagawa vor der Mündung des Karasawa	6
15	Adusagawa nach der Mündung des Tokusawa	10
16	Adusagawa bei der Brücke Kappabasi	15.5
17	Adusagawa bei Nakanoyu-Therme	22
18	Adusagawa bei der Bahnstation Simasima	49

	Tageszeit, am 19. Aug. 1941	Lufttemperatur, °C.	Flusstemperatur, °C.	*p*H	Dichteunterschied, γ
10	8^h 50	17.0	—	6.2	$+0.2_9$
11	8^h 30	17.0	14.1	5.8	-1.8_4
12	9^h 55	21.6	6.7	8.6	-1.7_5
13	10^h 30	20.8	7.0	7.4	-1.3_6
14	11^h 0	22.1	11.9	7.0	-1.0_5
15	12^h 30	22.3	11.1	6.9	-1.0_1
16	14^h 20	23.7	11.3	6.6	-1.4_0
17	16^h 25	23.4	18.1	7.0	-1.0_5
18	19^h 10	25.0	16.2	7.0	-0.3_1

Von 10 bis 13: Einzugsgebiet des Karasawa, der 4.5 km. von seinem Ursprung entfernt in den Adusagawa mündet.

Die genannten Orte zeigt Abb. 2.

Daneben ist eine Folge von Dichtemessungen an verschiedenen Flusswässern, die ich bei Studienreisen nach Thermal- oder Mineralquellen gesammelt habe, in Tabelle 4 aufgeführt.

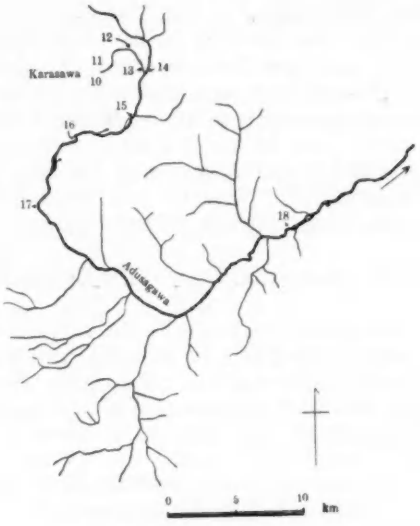

Abb. 2. Adusagawa-Fluss.

Tabelle 4. Dichteunterschiede zwischen Bach- und Flusswässern und dem Standard-Leitungswasser.

	Name des Gewässers	Ort	Entfernung vom Ursprung, km	Zeit	Wassertemperatur, °C.	Dichteunterschied, γ
19	Bächlein	bei Fumarole von Shonnazawa(2)	0	24. Mai 1939, 13h.....	—	− 0.9
20	Bächlein	bei kohlensäurehaltiger Mineralquelle Ippōsui(1)	1	4. Aug. 1938	14.7	− 1.3
21	Sendatugawa	bei Ganiba-Therme(2)	4	24. Mai 1939, 16h.....	8.0	− 1.1
22	Hontanigawa	bei Mineralquelle A_5 von Masutomi(3)....	6	8. Juli 1939, 11h.....	16.0	− 0.4
23	ebenda	ebenda	6	20. Okt. 1940, 17h.....	10.9	− 0.6
24	Kamasegawa	bei Mineralquelle E von Masutomi(3).....	7	19. Okt. 1940, 17h.....	12.5	− 0.4
25	Gamadagawa	bei Hotaka-Therme(1)	11	3. Aug. 1938	11.5	− 1.3
26	ebenda	bei Yarimi-Therme(1)	12.5	ebenda	14.0	− 1.9
27	Adusagawa	bei der Brücke Kappabasi	15.5	28. Juli 1939	10.1	− 1.6
28	ebenda	ebenda	15.5	13. Aug. 1940	9.9	− 0.8

(2) S. Oana, *J. Chem. Soc. Japan*, **60** (1939), 1008.
(3) S. Oana, ebenda, **15** (1940), 485.

Erörterung der Ergebnisse. Bei der Behandlung des vadosen Wassers gehen wir vom Wasserdampf in der Atmosphäre aus. Er weist eine verhältnissmässig geringe Konzentration an schweren Wasserisotopen auf. Nach M. Dole beträgt sein Dichteunterschied $-1.9_5\gamma$ und wird auf die Austauschreaktion zwischen O^{18} im Wasserdampf und $O_2{}^{16}$ in der Luft zurückgeführt.(4) Das heisst, bei dem sich ergebenden Gleichgewichte wächst die Gleichgewichtskonstante, die bei 0°C. 1.048 ist, mit dem Fallen der Temperatur(5); demnach soll der Dichtewert bei tieferen Temperaturen in den oberen Luftschichten wahrscheinlich sein.

$$O_2{}^{16} + 2H_2O^{18} \text{ (gasförmig)} \rightleftarrows O_2{}^{18} + 2H_2O^{16} \text{ (gasförmig)}$$

Wasserdampf kondensiert in der Luft in verschiedenen Formen. Er erscheint uns als Wolke, Nebel, Schnee oder Regen u.a.m. Auf dem Berggipfel von Fujisan, der sich 3776 m. über dem Meeresspiegel erhebt, wurden zwei Rauhreifproben gewonnen, die auf Grund meiner Prüfung die in Tabelle 5 mitgeteilten Werte zeigten.

Tabelle 5. Dichteunterschied zwischen dem Rauhreif und Standard-Leitungswasser.

Rauhreif	Zeit der Entstehung	Lufttemperatur, °C.	Luftdruck, mm Hg.	Dichteunterschied, γ
Rauhfrost	von 15^h am 16. Dez. 1941 bis 9^h am 17. Dez.	−18.6	496	-1.8_4
Rauheis	alt	erheblich höher		-0.3_9

Wenn unterkühlte Wassertropfen an irgend einen Körper anstossen, so entsteht Rauhreif. Bei tieferer Temperatur gebildeter Rauhreif ist undurchsichtig, weil er eine grosse Anzahl von kleinen Luftblasen enthält, und wird Rauhfrost genannt, während bei höherer Temperatur gebildeter eine durchsichtige Masse von Eis ist. Der letztere wird Rauheis genannt. Infolge der Schmelzwärme können sich die Wassertropfen in diesem Fall aber nicht vollständig in Rauhreif verwandeln, ein gewisser Anteil wird vielmehr stets als Wasserdampf an die Luft abgegeben. Mit steigender Lufttemperatur nimmt dieser fliehende Anteil zu. Dies ist wohl die Ursache dafür, dass Rauhfrost leichter ist als Rauheis, da bei der Tieftemperaturverdampfung Fraktionierung der Wasserisotopen in beträchtlicherem Grade stattfindet. Es ist deshalb über alle Erwartung schwierig, die Dichte des Wasserdampfes in der Luft durch Rauhreif zu ermitteln.

Wie verhält sich Schnee- oder Regenwasser? Am östlichen Abhang des Berges Norikuradake in Sinano-Provinz, sich etwa 1700 m. über die Meeresfläche erhebend, befindet sich eine kleine Hütte, die der Kaiserlichen Universität zu Tokio gehört. Ich habe im Vorgarten dieser Hütte Gelegenheit gehabt, den Schnee, der vom Nachmittag am 31. Dezember im Jahre 1941 bis zum Morgen am 2. Januar im Jahre 1942 bei Windstille gefallen war und 26.4 cm. hoch lag, in zwei gleich dicke Schichten getrennt

(4) M. Dole, *J. Chem. Phys.*, **4** (1936), 778.
(5) H. C. Urey und L. J. Greiff, *J. Am. Chem. Soc.*, **57** (1935), 321.

zu gewinnen. Die Dichtewerte der Oberschicht und der Unterschicht zeigt Tabelle 6.

Tabelle 6. Dichteunterschied zwischen Schnee und Standard-Leitungswasser.

	Zeit des Schneefalls	Lufttemperatur, °C.	Art der Schicht	Dichteunterschied, γ	
					durchschnittlich
Schnee am Abhang von Norikuradake	vom Nachmittag des 31. Dez. 1941 bis zum Morgen des 2. Jan. 1942	zwischen −8.3 und −11.0	obere 13.2 cm	-3.5_5	-2.7_9
			untere 13.2 cm	-2.0_2	

Der Dampfdruck des Eises ist bei tiefer Temperatur ausserordentlich klein und beträgt bei −10°C. nur 1.95 mm. Hg. Die in Tabelle 6 angegebene Dichte $-2.7_9\ \gamma$ können wir deshalb natürlich als die des Wasserdampfes in der Luft betrachten, weil der Schnee bei dem Fallen durch den Lufraum fast allen Wasserdampf aufnehmen muss. Die Ursache dafür, dass die obere Schicht leichter ist als die untere, wird wohl durch Fraktionierung der Wasserisotopen bei der Bildung des Schnees zu erklären sein. Es ist möglich, dass sich schwerere Wasserisotopen früher kondensieren als leichtere. Dass die Dichte des Regenwassers gegen Ende des Regenfalls geringer wird, wurde tatsächlich in Osaka bei einem Regenfall beobachtet.[6]

Beim Regenwasser sind die Dichteverhältnisse ebenso verwickelt wie beim Rauhreif. Als Dichte des Regenwassers wurden von jedem Autor bisher verschiedene Werte angegeben.[7] Sie liegen zwischen $-0.4\ \gamma$ und $-2.3\ \gamma$.

Flusswasser wird von obengenannten verschiedenen Niederschlägen geliefert, und seine Dichte ist in der ersten Laufstrecke klein, wie die Tabellen 2, 3 und 4 zeigen. Die Dichte nimmt dann mit der Länge der zurückgelegten Laufstrecke zu. Dieser Umstand dürfte auf die Fraktionierung der Wasserisotopen bei der Verdampfung des Flusswassers zurückzuführen sein. Es ist durchaus zu erwarten, dass sich die Konzentrationen der schweren Wasserisotopen im Wasser durch Verdampfung vergrössern, weil der Dampfdruck der schweren Wasserisotopen kleiner als der von H_2O^{16} ist. Die Dichte des Tamagawa-Flusswassers erreicht $0\ \gamma$ nachdem es sich etwa 53 km. von seinem Ursprunge entfernt hat. Dass in der Tabelle 2 Nr. 1 schwerer als Nr. 2 ist, wird dadurch erklärt, dass bei Nr. 1 im Vergleich mit Nr. 2 Verdampfung in höherem Grade wirksam war, da Nr. 1 am Abend Nr. 2 jedoch früh am Morgen entnommen wurde.

Warum bleibt dieser Wert $0\ \gamma$ im weiteren Flusslaufe nunmehr unverändert? Im Flusswasser wird wohl zwischen O^{18} im Wasser und $O_2{}^{16}$ in der Luft eine durch folgende Formel gezeigte Austauschreaktion stattfinden.[5]

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(6) M. Harada und T. Titani, Dieses Bulletin, **10** (1935), 206.

(7) Ebenda.
Y. Shibata, K. Noguchi und S. Kaneko, *J. Chem. Soc. Japan*, **58** (1937), 1013.
N. Parraaano, *"Atti del X° Congr. Intern. Chimica"*, II.
S. Oana, *J. Chem. Soc. Japan*, **60** (1939), 1005.

$$O_2^{16}+2H_2O^{18}\ (\text{flüssig}) \rightleftarrows O_2^{18}+2H_2O^{16}\ (\text{flüssig})$$

Die Gleichgewichtskonstante ist bei 0°C. 1.020 und bei 25°C. 1.012. Daneben wird wohl auch die Austauschreaktion, die zwischen O^{18} im Wasser und CO_2^{16} in der Luft nach folgender Formel stattfindet, mitwirken[5].

$$CO_2^{16}+2H_2O^{18}\ (\text{flüssig}) \rightleftarrows CO_2^{18}+2H_2O^{16}\ (\text{flüssig})$$

Die Gleichgewichtskonstante ist bei 0°C. 1.033 und bei 25°C. 1.028. Diese Austauschreaktionen verkleinern die Dichte des Flusswassers. Sie werden offenbar umso stärker wirksam, je länger der Flusslauf ist, weil sich die Substanz, die bei diesen Austauschreaktionen als Katalysator wirkt, nach dem Unterlauf hin vermehrt. Ich meine, dass die Dichte des Flusswassers in demjenigen Zustand, in dem die Zunahme der Dichte durch Verdunstung und die Abnahme der Dichte durch Austauschreaktionen sich gegenseitig ausgleichen, 0 γ ist.

Flusswasser fliesst schliesslich ins Meer hinein. Hier unterliegt es einer Verdunstung grössten Ausmasses, die den weitaus überwiegenden Anteil des atmosphärischen Wasserdampfes liefert. Die Dichte des Meerwassers ist deshalb gross, weil ihre Abnahme durch Austauschreaktion gegenüber der dauernden Zunahme durch Verdunstung fast wirkungslos bleibt. Tabelle 7 bringt den Dichtewert des Meerwassers, das von der Japanischen Ozeanographischen Gesellschaft (Nippon Kaiyô Gakkai) für Standard-Meerwasser festgesetzt wurde.[8]

Tabelle 7. Dichteunterschied zwischen Standard-Meerwasser und Standard-Leitungswasser.

	Dichteunterschied
Standard-Meerwasser Nr. 16	$+4.2_8\,\gamma$

Vorliegende Eröterung über Dichtewerte verschiedener vadoser Wässer zeigt, dass vom atmosphärischen Wasserdampf ausgehend und den Flusslauf folgend bis ins Meer die Wasserdichte sich vergrössert. Aus dieser Mitteilung folgt weiter, dass Flusswasser bei Dichtemessungen —jedenfalls in Japan—als Standard brauchbar ist, nachdem es vom Ursprunge des Flusses etwa 50 km. Laufstrecke zurückgelegt hat.

Es sei mir gestattet, Herrn Prof. Yuji Shibata und Herrn Prof. Kenjiro Kimura für ihre freundliche Anleitung und ihre Ratschläge und der Kaiserlichen Akademie der Wissenschaft für ihre finanzielle Unterstützung bei der Ausführung dieser Arbeit meinen herzlichen Dank auszusprechen.

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(8) *J. Oceanographical Soc. Japan*, **1** (1942), 95.

Die Kinetik der Umlagerung der Cis-Trans-Isomeren im Gaszustand (Dritte Mitteilung). Die Umlagerung der Dichloräthylene unter Einwirkung der Gefässwand und metallischen Katalysatoren.

Von Bunichi TAMAMUSHI.

(Eingegangen am 21. Mai 1942.)

Die Frage über die Homogenität der Umlagerungsreaktion von Cis-Dichloräthylen in Trans-Dichloräthylen bzw. der Gegenreaktion von Trans-Dichloräthylen in Cis-Dichloräthylen im Gaszustand ist in bisherigen Untersuchungen teilweise beantwortet aber quantitativ noch nicht erschöpfend dargelegt worden. R. Büll[1] hat in seiner grundlegenden Arbeit gezeigt, dass die Umlagerungsreaktion von Cis-Dichloräthylen in Trans-Dichloräthylen im Gaszustand von den angesetzten kleinen Glaskugeln, sowie von Platinschnitzeln bei der Temperatur 300°C. kaum katalysiert wird, sodass die Reaktion praktisch als homogen angesehen werden kann, während sich die Gegenreaktion von Trans-Dichloräthylen in Cis-Dichloräthylen auch bei niedereren Temperaturen gegen katalytische Einflüsse von Glaswänden als viel empfindlicher erweist. Neuerdings kamen Jones und Taylor[2] in ihrer kinetischen Untersuchung der thermischen Isomerisierung von Trans-Dichloräthylen in Cis-Dichloräthylen zur Schlussfolgerung, dass diese Reaktion möglicherweise zu einem gewissen Teil heterogen verläuft, aber doch annähernd als homogen angesehen werden kann, während die Nebenreaktion—die thermische Zersetzungsreaktion—weitgehend empfindlich gegen den Einfluss von der Gefässwand ist. Als Fortsetzung und Erweiterung unserer Untersuchungen[3] über die Kinetik der Umlagerung der Cis-Trans-Isomeren im Gaszustand haben wir nun in der vorliegenden Arbeit die Kinetik der Umlagerung von Cis-Dichloräthylen in Trans-Dichloräthylen sowie der Gegenreaktion von Trans-Dichloräthylen in Cis-Dichloräthylen im Gaszustand unter Einwirkung von der Gefässwand und metallischen Katalysatoren (Platin-Netz, Platinschwarz) untersucht. Die dabei erhaltenen Ergebnisse sollen in Bezug auf die Frage der Homogenität der genannten Reaktionen quantitative Angaben darbieten.

Die kinetischen Messungen wurden hier bei einer tieferen Temperatur, nämlich, bei 200°C. bzw. 180°C. durchgeführt, wodurch man die Möglichkeit bekam, die Pyrolyse der Reaktionsteilnehmer auszuschliessen. Zur kinetischen Messung wurde die statische Methode angewandt, worüber die vorhergehende Mitteilung berichtet hat. Das Reaktionsgefäss von

(1) L. Ebert und R. Büll, *Z. physik. Chem.*, A **152** (1931), 451; R. Büll, Dissertation. Würzburg, 1936.

(2) J. L. Jones und R. L. Taylor, *J. Am. Chem. Soc.*, **62** (1940), 3480.

(3) B. Tamamushi und H. Akiyama, *Z. Elektrochem.*, **45** (1939), 72: B. Tamamushi, H. Akiyama und K. Ishii, ebenda, **47** (1941), 340.

Terexglas betrug etwa 1 oder 2 Liter Inhalt, einmal ohne und ein anderesmal mit vielen Glasröhrchen oder mit einem Platin-Netz oder mit einer kleinen Menge von Platinschwarz. Ein Gefäss mit innerlich versilberter Wand wurde auch zur Messung verwendet. Der Druck des reagierenden Stoffes im Reaktionsgefäss wurde gleich etwa 30 mm. bzw. 40 mm. Hg. gesetzt.

Das zur Untersuchung verwendete Material wurde folgenderweise hergestellt: Cis- und Trans-Dichloräthylen wurden aus Dichloräthylen des Handels (Präparat von Schering-Kahlbaum) durch wiederholte Fraktionierung mittels einer Youngschen Kolonne dargestellt. Die getrennten Fraktionen hatten folgende physikalische Konstanten.

Tabelle 1. Physikalische Konstanten der isomeren Dichloräthylene.

	Trans-Isomer	Cis-Isomer
Siedepunkt	48–49° (752 mm.)	59.5–60.1° (760 mm.)
Dichte d_4^{25}	1.1187	1.1417
Brechungsindex n_D^{25} . . .	1.44316	1.44607
Dipolmoment	0.77×10^{-18}	1.81×10^{-18}

Das Platinschwarz wurde nach der Methode von Ramsay, Mond und Shields[4] hergestellt, dessen Aktivität man im voraus mit Hilfe der Hydrierungsreaktion von Benzol in Zyklohexan festgestellt hatte.

Das verwendete Platin-Netz hatte eine Dimension von 56.26 cm.^{2} und das Oberfläche-Volum-Verhältnis von dem von Glasröhrchen freien Gefäss und von dem mit Glasröhrchen gefüllten war 0.364 cm.$^{-1}$ bzw. 9.96 cm.$^{-1}$

Das Reaktionsprodukt wurde nach der Reaktionszeit in einer mit dem Reaktionsgefäss verbundenen Ampoule mittels Kohlendioxyd-Toluol-Gemisch möglichst rasch kondensiert und dann auf den Gehalt von Cis- oder Trans-Verbindung hin analysiert, indem man hierzu die Bestimmung der Dielektrizitätskonstante der benzoligen Lösungen anwendete. Die Standard-Beziehung zwischen der Dielektrizitätskonstante (abgekürzt DK) und den Zusammensetzungen ist schon in unserer vorhergehenden Mitteilung[5] angegeben worden.

Die untersuchten Reaktionen: Cis → Trans sowie Trans → Cis erreichen ein bestimmtes Gleichgewicht und zwar bei der hier gewährten Temperatur, nämlich bei 200°C. langsam nach mehr als 50 Stunden. Die Gleichgewichtslage konnte man nach den bisherigen Angaben wie unten annähernd abschätzen. Die Geschwindigkeitskonstante k (Cis → Trans) bzw. k' (Trans → Cis) hat man demgemäss mit Hilfe der folgenden Gleichungen:

$$k = \frac{K}{t(1+K)} \ln\left[\frac{100}{100-\left(1+\frac{1}{K}\right)c'}\right]$$

$$k' = \frac{K'}{t(1+K')} \ln\left[\frac{100}{100-\left(1+\frac{1}{K'}\right)c}\right]$$

(4) W. Ramsay, L. Mond und J. Shields, *Phil. Trans.*, **186** A (1895), 661.
(5) *loc. cit.* (3).

berechnet, wobei t die Reaktionszeit, K bzw. K' die Gleichgewichtskonstante ($K = \text{Trans}_\infty/\text{Cis}_\infty$, $K' = \text{Cis}_\infty/\text{Trans}_\infty$), und c (%-Cis) bzw. c' (%-Trans) das Gewichtsprozent des entstandenen Reaktionsproduktes bedeutet. Hierbei wurde natürlich angenommen, dass die beiden Cis→Trans und Trans→Cis Reaktionen unimolekular verlaufen.

Nach den Angaben unserer vorhergehenden Untersuchung wird die Gleichgewichtslage bei 200°C. als etwa 60%-Cis-Verbindung ermittelt, während sie nach den neuen genaueren Angaben von Wood und Stevenson[6] als 63.38%-Cis bei 185°C. und 62.2%-Cis bei 215°C. festgelegt ist. Wir haben demnach hierfür einen wahrscheinlichen Wert 62%-Cis dementsprechend $K=38/62$ bzw. $K'=62/38$ bei 200°C. angenommen. Die Ergebnisse der Messungen werden in folgenden Tabellen zusammengestellt.

Tabelle 2. Die Kinetik der Reaktion: Cis → Trans bei 200°C.

Versuchs-Nr.	Zeit in Stunden	Druck des Substrates (mm.)	DK	Reaktionsprodukt (%-Trans)	$k.10^6$ sek.$^{-1}$
		Im Gefäss ohne Katalysator.			
70′	3	29	2.496	8.0	7.88
71′	5	29	2.490	11.0	7.22
72′	9	29	2.478	16.5	6.68
20	3	40	2.495	8.5	8.91
19	5	40	2.485	13.0	8.84
					(8.07)
		Im Gefäss mit Glasröhrchen.			
60	3	40	2.500	7.5	7.75
59	5	40	2.485	13.0	8.84
61	9	29	2.473	18.6	7.89
					(8.16)
		Im Gefäss mit Platin-Netz.			
10	4	40	2.491	11.0	9.02
12	6	40	2.485	13.0	7.37
11	8	40	2.473	18.6	8.87
14	10	40	2.469	21.4	8.74
					(8.50)
		Im Gefäss mit versilberter Wand.			
40	2	40	2.502	5.8	8.00
38	4	40	2.493	9.4	7.50
41	6	40	2.485	14.0	7.54
					(7.68)
		Im Gefäss mit Platinschwarz (bei 180°C).			
82	1	40	2.483	13.9	48.1
84	2	40	2.480	15.8	28.4
83	3	40	2.475	18.5*	23.5
					(33.3)
		Im Gefäss mit Platinschwarz (bei 200°C).			
81	1/2	40	2.478	16.0*	123
80	4	40	2.430	39.0*	—

* Es trat dabei die Pyrolyse hervor.

(6) R. E. Wood und D. P. Stevenson, *J. Am. Chem. Soc.*, **63** (1941), 1650.

Tabelle 3. Die Kinetik der Reaktion: Trans → Cis bei 200°C.

Versuchs-Nr.	Zeit in Stunden	Druck des Substrates (mm.)	DK	Reaktionsprodukt (%-Cis)	$k'.10^6$ sek.$^{-1}$
		Im Gefäss ohne Katalysator.			
85′	10	27	2.351	24.5	8.66
83′	24	27	2.382	39.0	7.11
84′	50	28	2.425	59.0	10.33
1	2	40	2.314	6.5	9.54
3	4	40	2.323	11.0	8.41
2	6	40	2.332	14.8	7.83
					(8.84)
		Im Gefäss mit Glasröhrchen.			
5	2	40	2.312	5.5	8.00
7	4	40	2.323	11.0	8.41
6	6	40	2.340	18.5	10.16
8	8	40	2.343	20.3	8.54
					(8.78)
		Im Gefäss mit Platin-Netz.			
13	2	40	2.314	5.5	8.00
17	4	40	2.332	14.8	11.8
16	6	40	2.340	18.5	10.16
15	8	40	2.347	22.1	9.49
18	10	40	2.360	27.8	10.5
					(9.99)
		Im Gefäss mit versilberter Wand.			
49	2	40	2.316	7.5	11.1
46	6	40	2.341	19.4	10.8
47	8	40	2.355	25.9	11.6
48	10	40	2.351	24.2	8.5
					(10.5)
		Im Gefäss mit Platinschwarz (bei 180C°).			
88	1/2	40	2.326	12.0*	74
86	1	40	2.371	33.2*	132
87	2	40	2.408	50.8*	148
					(118)

* Es trat dabei die Pyrolyse hervor.

In Anbetracht dessen, dass man bei der Analyse des Reaktionsproduktes einen merklichen experimentellen Fehler nicht umgehen kann, so schwanken die k-Werte mehr oder weniger in einer Messungsreihe. Die Genauigkeit des Experiments könnte doch noch erhöht werden, es mangelte uns aber leider das Versuchsmaterial um den Versuch zu wiederholen.

Vergleicht man nun die oben erhaltenen k-Werte (Mittelwerte in jeder Messungsreihe) in den verschiedenen Messungsreihen miteinander, indem man den möglichen experimentellen Fehler in Betracht zieht, so muss man schliessen, dass die Reaktion: Cis-Verbindung → Trans-Verbindung durch die Einfüllung von Glasröhrchen oder durch die Versilberung der Gefässwand praktisch kaum beeinflusst wird, sodass die Reaktion als genügend homogen angesehen werden kann. Die katalytische Einwirkung vom Platin-Netz ist auch unbemerkbar, dagegen ist die Ein-

wirkung von aktivem Platinschwarz ganz bedeutend. Beim Zusatz von Platinschwarz tritt ausserdem die thermische Zersetzungsreaktion sogar bei der untersuchten Temperatur 200°C. hervor, was man durch die plötzliche Druckerhöhung im Reaktionsgefäss oder durch die Feststellung von entstandenem HCl im Reaktionsprodukt erkennen konnte. Bei 180°C. trat die Nebenreaktion in geringerem Masse auch bei Vorhandensein von Platinschwarz hervor.

Aus Tabelle 3 sieht man, dass auch die Reaktion: Trans-Verbindung →Cis-Verbindung unter Zusatz von Glasröhrchen nicht merklich beeinflusst wird, sodass man sie auch praktisch als homogen betrachten kann.

Diese letzte Reaktion scheint allerdings nach den oben erhaltenen Angaben gegen Platin sowie gegen Silberwand einigermassen empfindlich zu sein; ihre katalytische Einwirkung ist aber noch nicht sicher festzustellen. Die katalytische Wirkung von Platinschwarz ist auch in diesem Fall sehr bedeutend und zwar tritt die Zersetzungsreaktion schon bei 180°C. sogar auch in kürzerer Reaktionszeit hervor. Es ist also wahrscheinlich, dass der Isomerisierungsprozess an sich auch in diesem Fall praktisch genügend homogen ist, während die Nebenreaktion durch die Gefässwand oder metallische Katalysatoren weitgehend katalysiert wird[7].

Zusammenfassung.

Die Umlagerungsreaktion von Cis-Dichloräthylen in Trans-Dichloräthylen und ihre Gegenreaktion wurden unter Einwirkung von der Gefässwand sowie von metallischen Katalysatoren im Gaszustand bei 200°C. kinetisch untersucht.

Es wurde festgestellt, dass sowohl die Reaktion von Cis-Verbindung in Trans-Verbindung als auch die Reaktion von Trans-Verbindung in Cis-Verbindung durch die Einfüllung von Glasröhrchen oder einem Platin-Netz in Reaktionsgefäss sowie durch die Versilberung von der Gefässwand nicht merklich beeinflusst werden, woraufhin diese beiden Reaktionen praktisch als homogen betrachtet werden können.

Durch aktives Platinschwarz werden die beiden Umlagerungsreaktionen weitgehend katalysiert, wobei gleichzeitig die thermische Zersetzung der Reaktionsteilnehmer als Nebenreaktion stattfindet. In der Reaktion von Trans-Dichloräthylen in Cis-Dichloräthylen ist diese Nebenreaktion besonders empfindlich gegen den Katalysator.

Das Experiment in dieser Untersuchung wurde unter eifriger Mitwirkung von Herrn H. Akiyama und später von Herrn K. Ishii durchgeführt, den beiden Herren ich hier meinen warmen Dank aussprechen möchte. Herrn Prof. Dr. J. Horiuti (Sapporo) bin ich für seine wertvollen Ratschläge zu grossem Dank verpflichtet.

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Tokyo, Itabasiku.
Musashi Hochschule, Nedzu Chemisches Laboratorium.

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(7) Vergl. Jones u. Taylor, *loc. cit.* (2).

The Addition of Hydrogen Bromide to Crotonic Acid in Carbon Tetrachloride Solution and the Oxygen Effect.

By Osamu SIMAMURA.

(Received April 17, 1942.)

Recent investigations on the addition of hydrogen halides to ethenoid compounds have centred in the abnormal addition of hydrogen bromide, in which oxygen, organic peroxides, and ferromagnetic metals such as reduced nickel and iron reverse the direction of addition which should otherwise follow the Markownikoff rule. The works in this field have been reviewed by J. C. Smith[1] from one point of view and by F. R. Mayo and C. Walling[2] from another. The view[3] developed in this laboratory concerning the oxygen effect on hydrogen bromide reacting with ethenoid compounds is supported by a series of the experimental facts which have been obtained with a variety of substances[4]. It has been established that a bromine atom delivered from hydrogen bromide by the action of oxygen in the presence of an ethenoid compound causes an abnormal addition by a chain mechanism, attaching itself to the double bond of the ethenoid compound to yield a free bromo radical, which reacts then with hydrogen bromide to give the final product of the addition reaction with regeneration of another bromine atom. In many cases of the abnormal addition the bromine atom is oriented to the carbon atom which would take up hydrogen in the normal addition, thus giving rise to the formation of an abnormal product different from the normal one. There are, however, no theoretical grounds to expect that such will be the case in all ethenoid compounds.

The nature of the substitution at the double bond is no doubt a factor to determine the direction of addition. Although the mechanism of the normal addition is still in controversy, if it is assumed that hydrogen halides behave as polar molecules when they add to olefins, the direction of addition will depend on the polarity of the double bond. According to Smith[5], R. Robinson suggested that the direction of addition of hydrogen bromide to olefins could be predicted from a knowledge of the directive powers of the relevant groups when attached to the benzene nucleus: As the ortho and para directing groups not conjugated with the benzene nucleus all force electrons towards the nucleus, they should do so in compounds of the type $CH_2 = CHX$, where consequently the normal product should be CH_3CHBrX, which agrees with the Markownikoff rule. With meta directing groups the reverse should be the case.

(1) J. C. Smith, *Chem. and Ind.*, **56** (1937), 833; **57** (1938), 461; *Ann. Reports*, **36** (1940), 219.
(2) F. R. Mayo and C. Walling, *Chem. Rev.*, **27** (1940), 351.
(3) Y. Urushibara, *J. Chem. Soc. Japan*, **60** (1939), 717.
Y. Urushibara and O. Simamura, this Bulletin, **14** (1939), 323.
(4) O. Simamura, *ibid.*, **15** (1940), 292.
(5) J. C. Smith, *Chem. and Ind.*, **57** (1938), 461.

This hypothesis seems to have been substantiated by a great number of experimental facts. However, M. S. Kharasch, E. H. Rossin and E. K. Fields[6] recently obtained 1,1,1,2-tetrachloropropane by adding hydrogen chloride to trichloromethylethylene, although they could not add hydrogen bromide under antioxidant conditions. This result agrees with the Markownikoff rule, but is not in accordance with what is predicted from Robinson's hypothesis, trichloromethyl being considered a meta directing group[7].

The orientation of the bromine atom in the abnormal addition is a different matter, perhaps more complex. It may reasonably be assumed that a free bromine atom is directed towards the carbon atom with the higher electron density[8]. Thus, for example, in allyl bromide, which is considered to be polarised as indicated below, in the symbols of the English school,

$$\overset{\curvearrowleft}{CH_2}=CH \leftarrow CH_2Br\,,$$

a bromine atom is directed towards the γ carbon atom to yield finally 1,3-dibromopropane, the abnormal product. The hypothesis is the more attractive in so far as it brings, in conjunction with the polarisation of the double bond as postulated by Robinson, the orientation of the hydrogen bromide in the normal addition and the reversal of it in the abnormal addition into a consistent correlation. That the hypothesis of the greater reactivity of the carbon atom with the higher electron density may sometimes fail is shown by the instance of trichloromethylethylene cited above. As the trichloromethyl group is meta directing when attached to the benzene nucleus, it attracts electrons to itself; therefore, according to the hypothesis the product should be 1,1,1-trichloro-2-bromopropane when the mechanism involving bromine atoms is in operation, whereas 1,1,1-trichloro-3-bromopropane was really obtained under oxidant conditions.[6]

Another view is suggested by F. R. Mayo and C. Walling[2] with additional advantages. The point of attack by the bromine atom is little affected by the polarity of double bond, but depends upon the relative stability of the two bromo radicals which may be formed. To exemplify the theory, allyl bromide gives 1,3-dibromopropane in the abnormal addition because the order of the stabilities is as follows,

$$CH_2Br\text{–}\dot{C}H\text{–}CH_2Br > \dot{C}H_2\text{–}CHBr\text{–}CH_2Br\,.$$

However, why the former radical is more stable than the latter remains to be explained. Perhaps the idea of hyperconjugation[9], i.e., conjuga-

(6) M. S. Kharasch, E. H. Rossin and E. K. Fields, *J. Am. Chem. Soc.*, **63** (1941), 2558.

(7) A. F. Holleman, J. Vermeulen and J. de DeMooy, *Rec. trav. chim.*, **33** (1914), 1. K. Lauer, *J. prakt. Chem.*, **142** (1935), 252.

(8) M. S. Kharasch, H. Engelmann and F. R. Mayo, *J. Org. Chem.*, **2** (1937), 288.

(9) See, for example, R. S. Mulliken, C. A. Rieke and W. G. Brown, *J. Am. Chem. Soc.*, **63** (1941), 41.

tion with saturated groups, would account for the assumed order of decreasing stabilities of aliphatic free radicals, tertiary>secondary> primary. In the tertiary radical the free valency electron can conjugate with three groups, while in the secondary one it can do so with two groups at most, thus the former being more stable by the energy acquired through the extra conjugation with the third additional group. From the same argument it is concluded that the secondary radical is more stable than the primary one.

The hypothesis of the radical stability could most satisfactorily explain the observations with crotonic acid[10] which gives always β-bromobutyric acid irrespective of the conditions of addition, because the β-bromo radical $CH_3\dot{C}HBrCHCOOH$ should be more stable than the α-isomeride, $CH_3CH\dot{C}HBrCOOH$, by virtue of the conjugation of the free valency electron with the carboxyl group. The formation of β-bromobutyric acid as a normal product is in accord with the prediction from Robinson's hypothesis.

Propenylbenzene[11] and cinnamic acid[12] are stated to give with hydrogen bromide always 1-phenyl-1-bromopropane and β-bromohydrocinnamic acid, respectively. Although a discussion of these findings seems to be rather hasty as the full experimental details are not available, they may be considered to indicate on the basis of the theory of the radical stability that the radicals $C_6H_5\dot{C}HBrCHCH_3$ and $C_6H_5\dot{C}HBrCHCOOH$ should be more stable than $C_6H_5CH\dot{C}HBrCH_3$ and $C_6H_5CH\dot{C}H_2COOH$, respectively. This is unexpected because theoretically the latter radicals should be more stable as the conjugation of the free valency electrons with phenyl groups would contribute much more to the stabilisation of the free radicals. Attention must be paid to another factor determing the orientation of hydrogen bromide in the abnormal addition. It concerns the reaction between the free bromo radical and hydrogen bromide where the final addition product and a bromine atom are yielded. When a free radical stabilised by the conjugation of the free valency electron with some groups reacts with hydrogen bromide, it would require a greater activation energy and consequently would react slower than when such stabilisation is absent. Then the reactivity of the free bromo radicals may be a predominant factor to determine the direction of addition of hydrogen bromide. Thus, those olefins with a phenyl group in conjugation with double bond may give results apparently contradictory to the theory of radical stability.

At this stage of development, where the problem of the orientation of hydrogen bromide has not reached a complete solution, accumulation of more experimental data is desirable.

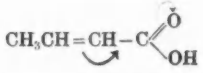
Addition of hydrogen bromide to crotonic acid has already been studied[10] with results that β-bromobutyric acid is the only product obtainable irrespective of the conditions of addition and there seems to

(10) C. Walling, M. S. Kharasch and F. R. Mayo, *J. Am. Chem. Soc.*, **61** (1939), 2693. D. C. Grimshaw, J. B. Guy and J. C. Smith, *J. Chem. Soc.*, **1940**, 68.

(11) Unpublished work of M. S. Kharasch, P. C. White and F. R. Mayo cited by F. R. Mayo and C. Walling, *Chem. Rev.*, **27** (1940), 351.

(12) A. Michael and G. H. Shadinger, *J. Org. Chem.*, **4** (1939), 128.

be no indication of the accelerated reaction under oxidant conditions. Walling, Kharasch, and Mayo suggested that the chain mechanism might not operate when the double bond is conjugated with a carboxyl group, but they did not exclude the possibility that both mechanisms, normal and abnormal, yield the identical product. Smith and co-workers[10] are of the opinion that bromine is not attracted to the α-carbon atom of crotonic acid since there is no accumulation of electrons in that position, the mesomeric polarisation in the molecule being such as represented by the formula.



As the action of the mixture of hydrogen bromide and oxygen on allyl bromide and certain other ethenoid compounds has proved to be a very useful method for elucidating the mechanism of the abnormal addition[3][4], the same method has now been applied to crotonic acid to determine whether a similar chain mechanism operates when hydrogen bromide is added to this acid under oxidant conditions.

Into a suspension of 10 g. of crotonic acid in 50 c.c. of carbon tetrachloride the mixture of hydrogen bromide and oxygen was passed in the dark. The reaction vessel was cooled with ice water throughout the passage of the gas mixture. At the end of three hours the reaction mixture was found to have deposited a few c.c. of a pale brown oil, which on treatment as described in the experimental part yielded α-hydroxy-β-bromobutyric acid, m.p. 97–98°C. The carbon tetrachloride layer was colourless and on removal of the solvent 17 g. of an oil was obtained. It was distilled under diminished pressure and the first fraction, which passed over at 122–127° at 18 mm., was redistilled to yield 4.85 g. of β-bromobutyric acid, b.p. 94–98° at 4 mm., n_D^{20} 1.4782. When this was solidified by cooling with ice and then gradually warmed, the last pieces of crystals disappeared at 14°. If any α-bromobutyric acid was formed, it would be present in the head fraction as it boils lower than the β-isomeride, and as this fraction melted at 14°, whereas the α-bromo-acid melts at –4°[13], it seems to have contained no appreciable amount of the α-isomeride. In the first distillation, as the temperature of the bath was raised, the thermometer reading rose continually from 127° and, when it reached 148°, the distillation was stopped as the distilling liquid solidified to a crystalline mass filling the arm of the distilling flask. The crystals were identified as crotonic acid dibromide, m.p. 86–88°. The residue in the flask also solidified on cooling to crystals of the same substance embedded in viscous oil. Thus the reaction products remaining in carbon tetrachloride were found to consist mainly of β-bromobutyric acid and crotonic acid dibromide. That α-bromobutyric acid was not detected is in accord with the findings of the foreign workers[10]. The formation of some substances of peroxidic nature is certain, although they were not identified, as the carbon tetrachloride solution and the brown oil liberated iodine from aqueous potassium iodide, while any of the three compounds isolated was found not to do so even when acidified with hydrochloric acid. Fur-

(13) Lespieau, *Compt. rend.*, **139** (1904), 739.

ther, crotonic acid dissolved in carbon tetrachloride and placed in diffuse light for a day developed no coloration with ferrous ammonium sulphate and ammonium thiocyanate. Thus it is concluded that reactions of the same type occurred as when the gas mixture was allowed to react with allyl bromide[3]. The formation of crotonic acid dibromide is a convincing evidence in support of the view that the reaction involved bromine atoms, which, in reacting with crotonic acid, must have attacked the β-carbon atom, as no α-bromobutyric acid or its derivatives were detected.

Isolation of α-hydroxy-β-bromobutyric acid was unexpected. If hydrogen peroxide or an organic peroxide formed[3] in the course of the reaction should yield with crotonic acid α, β-epoxybutyric acid, this would readily react with hydrogen bromide to give the hydroxybromobutyric acid as described in the experimental part. However, the observed formation of the hydroxybromobutyric acid may be adduced in substantiation of the view that the reaction involved the formation of the bromine atom and that the bromine atom attached itself to the β-carbon atom of crotonic acid. Then the formation of the hydroxybromo-acid is interpreted as follows: In the first place a β-bromo radical acid is formed by the combined action of hydrogen bromide and oxygen or by the action of a bromine atom on crotonic acid

$$2CH_3CH=CHCOOH+2HBr+O_2 \longrightarrow 2CH_3\underset{\displaystyle Br}{\underset{|}{C}}HCHBrCOOH+H_2O_2$$

$$CH_3CH=CHCOOH+Br \longrightarrow CH_3\underset{\displaystyle Br}{\underset{|}{C}}HCHBrCOOH\,.$$

This radical acid then reacts with oxygen or hydrogen peroxide formed to yield finally the acid under consideration.

Oxygen having been shown to cause the reaction involving bromine atoms, it was expected that it might more or less accelerate the addition reaction, and its effect on the rate was examined. Hydrogen bromide (0.0135 mole) was allowed to react with crotonic acid (0.0128 mole) in carbon tetrachloride (10 c.c.) in a glass tube with a capacity of 60 c.c. for three hours in the dark at room temperature either in presence or in absence of oxygen. From the reaction mixture carbon tetrachloride and the unreacted hydrogen bromide were removed under reduced pressure and the remaining oil was treated with a sodium hydroxide solution and analysed for liberated bromide ion. The extent of reaction of crotonic acid was calculated on the assumption that the liberated bromide ion gives the amount of β-bromobutyric acid formed and no other products were yielded at all. It is obvious from the results tabulated below, that, contrary to the expectation, oxygen did not exert any perceptible influence on the rate of the reaction when the amount of oxygen admitted was small. The extent of addition decreased slightly as the amount of oxygen was increased. That in these cases the side reaction involving oxygen as has been described above took place appreciably was demonstrated by the turbid appearrance of the reaction mixture when the greater part of the solvent was removed. No acceleration by oxygen of the addition of hydrogen bromide to crotonic acid might be taken to indicate that the bromo radical acid reacts readily with oxygen but not with hydrogen bromide to continue the chain reaction, which would superpose itself on the rapid

normal addition. There is indeed an incipient formation of chains by the joint action of hydrogen bromide and oxygen but they cannot develop to a noticeable abnormal addition reaction.

Table.

The Addition of Hydrogen Bromide to Crotonic Acid in the Presence of Oxygen in Carbon Tetrachloride Solution in the Dark.

Experiment Series	No.	Oxygen admitted mm. Hg	Crotonic acid reacted %	Temp.	Method of analysis*
I	1	0	66.9	19–20	a
	2	0	66.5		a
	3	36†	68.5		a, b
II	4	0	68.0	20	b
	5	47	68.2		b
	6	63	68.1		b
III	7	0	69.8	20	b
	8	157	66.7		b
	9	274	62.5		b

Crononic acid, 0.0128 mole; hydrogen bromide, 0.0135 mole; carbon tetrachloride, 10.0 c.c. Reaction time, three hours. Experiments belonging to the same series were conducted in quick succession.

* As regards the methods of analysis adopted see the experimental part.

† The amount of oxygen is 0.092 millimole.

Experimental Part.

Materials. Hydrogen bromide was generated by dropping bromine on hot tetralin, passed through a bottle containing cold tertalin and then through a tube filled with anthracene. It was dried by passage through a tube filled with glass wool sprinkled with phosphorus pentoxide and was conducted into a reaction vessel after mixing with oxygen which was taken from a cylinder and dried with phosphorus pentoxide. When the effect of oxygen on the extent of addition was investigated, the hydrogen bromide dried with phosphorus pentoxide was collected in a tube cooled with liquid air. It was melted, solidified again, and the tube was evacuated with a mercury diffusion pump. The process was repeated three times and the hydrogen bromide was fractionated, the middle portion being used. Crotonic acid was recrystallised from petroleum ether and the purified sample melted at 72–73°. Carbon tetrachloride was refluxed with an alkaline permanganate solution, dried with anhydrous calcium chloride, and fractionated after desiccation with phosphorus pentoxide.

The Action of the Mixture of Hydrogen Bromide Gas and Oxygen on Crotonic Acid in Carbon Tetrachloride in the Dark. The essential part of the experiment has already been described above. The pale brown oil which was deposited from the reaction mixture weighed 4.2 g. and, when a little water was added, complete solution took place. This was extracted with ether and the ethereal solution was dried with anhydrous sodium sulphate. On removing the ether under reduced pressure hexagonal plates insoluble in carbon bisulphide and very soluble in cold water were obtained. The product crystallized from water was dissolved in ether and by adding a little petroleum ether crystals melting at 97–98° were obtained; yield, 0.5 g. (Found: Br, 43.8. Calculated for $C_4H_7O_3Br$: Br, 43.6%). Its properties coincide with those

described for α-hydroxy-β-bromobutyric acid. According to P. Melikoff[14], when the sodium salt of α-hydroxy-β-halocarboxylic acid is boiled in aqueous solution, carbon dioxide splits off and aldehyde or ketone results according to the constitution of the original acid. The substance obtained here was dissolved in a dilute sodium carbonate solution and heated, when the characteristic odour resembling that of acetaldehyde evolved. Although it was not characterized by the formations of derivatives, there is no doubt that propionaldehyde was formed. The melting point of the substance was not depressed on admixture with an authentic specimen of α-hydroxy-β-bromobutyric acid prepared by the action of hydrogen bromide on α, β-epoxybutyric acid (methylglycidic acid).

α-Hydroxy-β-bromobutyric Acid from Methylglycidic Acid. Methylglycidic acid (0.3 g.) prepared from α-bromo-β-hydroxybutyric acid following the direction given by Melikoff[15] for α-chloro-β-hydroxybutyric acid was suspended in 25 c.c. of carbon tetrachloride and the mixture of hydrogen bromide and oxygen[16] was passed for an hour and a half. The acid changed into a sticky mass. The carbon tetrachloride was decanted and the product was crystallized from water, m.p. 96–98°.

The Effect of Oxygen on the Addition of Hydrogen Bromide to Crotonic Acid in Carbon Tetrachloride in the Dark. In a glass tube with a capacity of 60 c.c. 1.1 g. of crotonic acid and 10 c.c. of carbon tetrachloride were placed and the tube was connected to the vacuum line. To remove the oxygen the contents of the tube were solidified by cooling with liquid air and the tube was evacuated with a mercury diffusion pump. The contents were then melted, again solidified, and the tube evacuated. The procedure was repeated three times. Then 0.0135 mole of hydrogen bromide (0.5 c.c. of liquefied hydrogen bromide at the temperature of solid carbon dioxide) was condensed on the top of the solidified mixture and oxygen was introduced to a specified pressure. The tube was sealed off and shaken manually as uniformly as possible. After three hours the capillary tip of the reaction tube was connected to a pump by means of a piece of rubber tubing, the tip was broken by crushing it from outside and the remaining hydrogen bromide and the greater part of carbon tetrachloride were removed. The remaining oily product was transferred to a 50 c.c. Erlenmeyer flask, which was then placed in a desiccator containing potassium hydroxide and scraps of paraffin. The desiccator was evacuated for three hours and left overnight. The product (0.2–0.3 g.) was treated with 5 c.c. of 1N sodium hydroxide solution, heated for thirty minutes on a water-bath, and by adding silver nitrate to the solution acidified with dilute nitric acid silver bromide was precipitated and weighed. This method of analysis is referred to as (a) in the accompanying table. Another method (b) consisted in heating the sample with 5 c.c. of 1N sodium hydroxide solution for five minutes and titrating the liberated bromide ion by the Volhard method. Both methods were found to give the identical value when applied to the product of Exp. No. 3.

Summary.

(1) Hypotheses suggested to explain the orientation of hydrogen bromide in the addition to the ethenoid compound have been briefly reviewed and critisized.

(2) Allowing the mixture of hydrogen bromide and oxygen to react with crotonic acid in carbon tetrachloride, three products, β-bromobutyric

(14) P. Melikoff and Petrenko-Kritschenko, *Ann.*, **266** (1891), 370; *Chem. Zentr.*, **1890**, I, 524.
(15) P. Melikoff, *Ber.*, **16** (1883), 1270.
(16) For the preparation oxygen is not necessary.

acid, crotonic acid dibromide and α-hydroxy-β-bromobutyric acid, have been isolated.

(3) Oxygen has been found not to accelerate the addition of hydrogen bromide to crotonic acid in carbon tetrachloride solution in the dark.

(4) It is concluded that in the addition of hydrogen bromide to crotonic acid in the presence of oxygen, this participates in the reaction producing free bromo-radical.acid and bromine atoms, the latter being attached to the β-carbon atom of crotonic acid, but that the chains involving these cannot develop because of the ready reaction of the bromo radical acid with oxygen rather than with hydrogen bromide.

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Studies on the Adsorption at the Solid – Liquid Interface. IV. Relations among the Adsorption, the Oiliness and the Flocculation of the Powder.

By Hideo AKAMATU.

(Received April 24, 1942.)

Introduction. When the surface of a solid contacts with a liquid or some powder is immersed in a liquid, the property of the surface of solid is changed by the solvation or the adsorption of a certain substance from the solution. There are many phenomena which depend on such property of the surface of solid. The action of the lubricant or the flotation process is the example of the application of such phenomena. To explain those phenomena we always assume the adsorption layer on the surface of the solid material. In practice, however, it is troublesome to find the method of investigating the adsorption layer, for the amount of the substance adsorbed is very small and the effect is very sensitive. We get the informations, in many cases, by the indirect method or by the analogy to some other cases, for instance, by the behaviour of the monomolecular film on the surface of water.

In our laboratory, the effects of the liquids on the friction coefficient of the glass surface have been studied,[1] and moreover, some results were

(1) J. Sameshima and coworkers, this Bulletin, **11** (1936), 659, 791; **12** (1937), 96, 127; **13** (1938), 127, 134; **14** (1939), 270, 297; **15** (1940), 288, 467. J. Sameshima, H. Akamatu and T. Isemura, *Rev. Phys. Chem. Japan*, **14** (1940), 55.

obtained regarding the adsorption by glass.[2] The relations between those phenomena will be considered in the present report.

Summary of the Results on the Adsorption by Glass. The adsorptions by the glass powder of such substances as carboxylic acids, esters, nitrobenzene, aniline and chlorobenzene from their solutions dissolved in a non-polar solvent such as benzene or toluene were studied in the preceding papers.[2] The adsorbing behaviours can be classified into the following three groups.

(I) The compounds having carboxyl radicals were adsorbed selectively from their benzene or toluene solution by glass, and the adsorption took place readily in the region of the low concentration of the solution (e.g. in the order of 10^{-3} mol/l.). In these cases, the adsorption layer seemed to approach to the monomolecular layer and then saturate, except the compound having small molecular weight such as acetic acid, which was much adsorbed.

(II) Alcohols did not show such strong selective adsorption as carboxylic acids, and no remarkable adsorption has been observed in the region of the low concentration. When the concentration of the solution, however, was beyond a certain range (e.g. 10^{-2} mol/l.), the selective adsorption took place, and things were like to the case of carboxylic acids.

(III) In the case of nitrobenzene, aniline and chlorobenzene, notwithstanding their large dipole moments, any considerable selective adsorption was not observed even in the range of the pretty high concentration of the solution. Those results are shown schematically in Fig. 1.

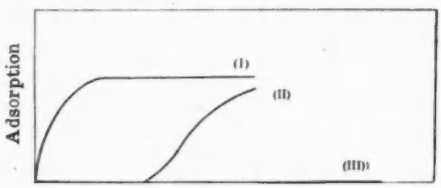


Fig. 1.

The relations between those results of the adsorption and the oiliness of liquids, and the flocculation or the apparent sedimentation volume of the powder in liquids will be discussed in the following sections.

Adsorption and Oiliness. The mechanism of the oiliness of the lubricant has not yet been understand thoroughly. However, two things, at least, are considered to be necessary. The first is the protecting action by the molecules of the lubricant combining with the surface of the solid. When the lubricant is pure liquid, this is caused by the solvation, and if the lubricant is a solution, it is necessary that the selective adsorption of a certain molecules take place. The adsorption is a necessary condition to reduce the friction, though it is not a sufficient one for good oiliness. For the second condition, the adsorption layer at the friction surface must have a special property to reduce the friction. As for this property, however, there is no definite theory. With regard to a certain homologous series of the lubricant, the larger the molecule, especially having the long

(2) H. Akamatu, this Bulletin, **17** (1942), 141, 161, 260.

hydrocarbone chain, the better the oiliness is. This is the most remarkable and suggestive fact. Things which are considered from this fact are as follows. (1) The shape of the molecule is associated with the good oiliness. Especially the flexibility of a molecule attracts the attention of the investigators. (2) The good orientation of molecules in the adsorption layer is necessary for good oiliness. As the lateral force between molecules oriented is greater, the adsorption layer will be more stable, by which the friction surface will be covered homogeneously. (3) The large molecules have the effect to separate the friction surfaces from each other. All of those things have the parallelism with the size or the length of the molecules. In the practical lubricating action, all of those things may be involved at the same time.

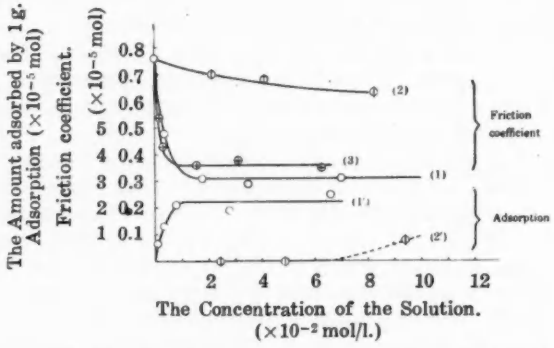
The adsorption is not a sufficient condition for good oiliness, while it is a necessary condition at least. For instance, fatty acids are readily adsorbed by glass in general. Among them, acetic acid seems to be most readily adsorbed, and consequently, it reduces more or less the friction coefficient of the glass surface, though it shows no remarkable oiliness. The friction coefficient of glass without any lubricant is almost unity. In the case of using acetic acid as lubricant, the friction coefficient is reduced to about 0.6; on the other hand, with more favourable fatty acids having long hydrocarbon chains, the values are far more small, with oleic acid, for instance, this value is 0.24.

Molecules, consisted of the hydrophilic radical and the hydrophobic radical at the same time, orient themselves at the surface of water in such a manner as their hydrophilic radical sets in water. This idea has been expanded to the surface of hydrophilic solid instead of water, and it is assumed that such molecules also orient themselves anchoring their polar groups on the solid surface and the adsorption takes place as the results. However, such an assumption cannot be applied imprudently to the case of the glass surface, at least, as mentioned above.

Among the polar radicals, the carboxyl radical is most readily adsorbed by the glass surface. This fact is consistent with the carboxylic acid, especially fatty acids, have much or less good oiliness. The fact[3] that the oiliness of toluene or xylene solution dissolving small quantity of fatty acid, was identical with the oiliness of the fatty acid itself independing on the solvent, has been understood by the assumption that the fatty acid is selectively adsorbed by the friction surface and that the friction depends on it only. This assumption is consistent with the experimental results that the fatty acids are always preferentially adsorbed by glass. Hydroxyl radicals, on the other hand, are not selectively adsorbed by glass so strongly as carboxyl radicals. The alcohols are adsorbed from their benzene solutions only at the high concentration of the solution. This relation has also been investigated from the oiliness of the solution containing alcohol. For instance, in the case of the xylene solution dissolving palmitic acid, the oiliness is pretty good in the range of the low concentration of the solution and as the concentration increases the oiliness approaches to a saturated value. On the other hand, the oiliness is not good in the case of the toluene solution containing tetradecyl alcohol, not-

(3) H. Akamatu, this Bulletin, **13** (1938), 127.

withstanding the good oiliness being anticipated from the molecular structure of tetradecyl alcohol. The reason is that tetradecyl alcohol does not adsorbed preferentially at the glass surface as palmitic acid. This relation is shown in Fig. 2. The considerable adsorption of tetradecyl alcohol does not take place until the concentration of the solution approaches to the saturation.



(1): Palmitic acid/Xylene (1′): Palmitic acid/Toluene
(2): Tetradecyl alcohol/Toluene (2′): Tetradecyl alcohol/Benzene
(3): Oleic acid/Toluene

Fig. 2.

Notwithstanding that the fatty acids and the alcohols have much or less good oiliness, their esters[4] have rather poor oiliness. This is also understood from their small adsorbability.

With regard to nitrobenzene, aniline and chlorobenzene, no notable selectivity against benzene has been observed, from the adsorption experiment. The reducing action of the friction of the glass surface by those substances[5] are also poor just as the action by benzene or toluene. For the bad oiliness of those substances, the deficiency in the flexibility of those molecules has been assumed by many investigators, however, this may be also caused by their bad adsorbability to the surface. Since benzoic acid is selectively adsorbed by glass and the xylene solution dissolving benzoic acid has also much or less good oiliness as compared with xylene itself. Friction coefficients of those substances are shown in Table 1.

Table 1.

Lubricant	Friction Coefficient
Benzene	0.78
Toluene	0.76
Xylene	0.76
Nitrobenzene	0.84
Aniline	0.73
Chlorobenzene	0.81
Xylene solution dissolving Benzoic acid (2%)	0.59

In the case when the lubricant is consisted of many components, the fact[3] that the oiliness of such a system depends on only a certain material alone, may understood from the consideration of the selective adsorption.

(4) T. Isemura, this Bulletin, **14** (1939), 270.
(5) T. Isemura, this Bulletin, **15** (1940), 288.

Adsorption and Flocculation of the Powder. It is well known that the stability or the swelling of the colloidal system depends on the nature of the dispersion medium. In the case when relatively large particles (microscopic) are suspended or sedimented in the liquid, the phenomena that the property of the system is affected by the nature of the liquid medium attract the attention of the investigators,[6] not only because of its importance for the application, but also the fact that the system may be considered as a model of a colloidal system.

It is remarkable that the flocculation and the sedimentation volume of the powders in various kinds of liquids varied with the nature of the liquid.[7] If the powder is hydrophilic, it is not liable to flocculate in the polar liquid, and the particles are dispersed, and consequently the sedimentation velocity is slow and the apparent sedimentation volume is small. On the other hand, in the non-polar liquid, the particles aggregate each other and become coarse particles, and consequently the sedimentation velocity is fast and the apparent sedimentation volume is large.

If the adhesion forces between the particles are strong, they aggregate each other by their contact points, and as the whole system they will take the loose packing, so the sedimentation volume will be large. On the other hand, if the adhesion forces are weak, the aggregation or the flocculation does not take place, and they will take the close packing as the whole system, and consequently the sedimentation volume will be small.

The aggregation of the particles may be prevented by the addition of some substances to the liquid even in the case of non-polar solvent, and as the results, the sedimentation volume of the system will be reduced. This phenomenon is remarkable and the addition of the substance to the solvent is analogous to the protecting action of the colloidal system. Taking the glass powder, for instance, this relation will be seen in Table 2.

Table 2.

Solvent	Solute		The ratio of the sedimentation volume of 1 g. powder.
Toluene	——	.....	1.00
Benzene	——	.....	1.00
Toluene	Oleic acid	(1%)	0.79
"	Palmitic acid	(2%)	0.82
"	Tripalmitine	(1%)	0.82
"	Benzoic acid	(1%)	0.88
"	Acetic acid	(5%)	0.94
Benzene	Palmitic acid	(0.02 mol/l.)	0.84
"	Nitrobenzene	(0.07 ")	1.00
"	Chlorobenzene	(0.07 ")	1.00

(6) Wo. Ostwald and W. Haller, *Kolloidchem. Beihefte*, **29** (1929), 354; P. Rehbinder, *Z. physik. Chem.*, A **146** (1930), 63; Bloomquist and Schutt, *Ind. Eng. Chem.*, **32** (1940), 827; K. Suzuki, *J. Chem. Soc. Japan*, **62** (1941), 888; B. Tamamushi and S. Tomatsu, this Bulletin, **17** (1942), 23.

(7) H. Akamatu, this Bulletin, **13** (1938), 456.

In those cases, when the substance added to the solvent can be adsorbed selectively by glass, there are much or less reducing effect of the sedimentation volume. Nitrobenzene or chlorobenzene has no effect. This relation is quite like the case of the oiliness. The preventing action of the aggregation of the particles and the reducing action of the friction of the solid surface by the so-called surface active substances is quite parallel in each other. This fact shows that the adhesion force between the particles is the same sort with the friction force. A series of the studies by Búzagh[8] on the "Abreisswinkel" also showed the analogous results.

The peculiar behaviour of the float, frequently experienced during the density measurement by the float method, seems to have some relation to the adhesion force between particles. As already described in the preceding paper,[9] this phenomenon is as follows. In the non-polar liquid such as benzene or in the solution dissolving the non-adsorbable solute, the float occasionally moves laterally toward the wall of the cell and attaches to it. In the benzene solution dissolving the surface active substance, however, this behaviour does not occur in general. This phenomenon seems to be related to the aggregation of the particles of the powder. We may suppose, from this fact, that the aggregation takes place not only when the particles collide each other by the chance, but also when they approach each other by some attraction force in the liquid such as benzene or toluene.

In conclusion the author wishes to express his hearty thanks to Prof. Jitsusaburo Sameshima for his kind guidance and encouragement. The cost of this research has been defrayed from the Scientific Research Encouragement Grant from the Department of Education, to which the author's thanks are due.

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(8) A. von Búzagn, "Kolloidik", 1936, Dresden, p. 158; *Kolloid-Z.*, **85** (1938), 318.

(9) H. Akamatu, this Bulletin, **17** (1942), 260.

Physico-Chemical Investigations on Catalytic Mechanism. VI. On the Fischer-Tropsch Synthesis of Hydrocarbons. (Experimental Series II)*** (2).

By Senzo HAMAI.

(Received January 14, 1942.)

The present paper being a further report of the series of investigations[1], we shall omit the experimental aspects, but we attempt to describe the results concerning the effects of promoters on the Co type catalyst. Experimental apparatus and detailed experimental procedures have been fully presented in our previous paper[2].

One of the most interesting problems in the catalytic mechanism which have not yet been settled is the role of promoters in the catalytic activity in general. Bearing these in mind, we have carried out the experiments which may possibly throw some light in correlation with the catalytic activity; furthermore, these experimental results clear the way for the systematic explanations of the mechanism. So far many investigators[3] have undertaken the task and contributed much, but on account of the fundamental difficulty to get reproducible results, most experimental results can hardly be considered as reliable as to give a clear-cut, general conclusion. In this sense, we are justified to say that, in such chaotic conditions of numerous results, we are confronted practically with a hopeless situation. For such reasons, the author considers that every bit of experimental results has to be correlated in some such systematic manner as to enable us to get hold of a clear vision of the catalytic mechanism out of such chaotic mass of numerous investigations.

We mainly present the effects of B_2O_3 in our new catalyst and of Cu, the combined effects of ThO_2 and CeO_2, as well as those of pre-treatments of the catalysts.

Experimental Results. The catalyst which we had employed was a series of the catalysts of Co with various promoters such as CeO_2, ThO_2, B_2O_3, and Cu and Kieselguhr as a carrier (support), as shown in our tables; and the method of preparation and experimental procedures were exactly similar to those, already described in our report IV[4].

(***) Most of the results given in this paper was obtained and completed in 1939–1940, but the publication of them has been withheld.

(1) Our reports; I, II, III, IV, and V.
(I) *J. Chem. Soc. Japan*, **62** (1941), 516;
(II) This Bulletin, **16** (1941), 213;
(III) *J. Soc. Chem. Ind. Japan*, **45** (1942), 313;
(IV) This Bulletin, **17** (1942), 166;
(V) This Bulletin, **17** (1942), 252.

(2) Report IV, this Bulletin, **17** (1942), 166.

(3) Series of papers by the schools of Fischer, Kita, and others.

(4) Report IV, this Bulletin, **17** (1942), 166.

Tables 1–4 indicate typical results out of various experiments. As seen in Table 1, the effects of B_2O_3 on the average gas contraction as an approximate measure of the catalytic activity are well detectable. It seemed that the addition of B_2O_3 improved the activity as well as the quality of the products[5]; i.e., in $F_{40}(A)$–$F_{40}(G)$ series where the catalyst

Table 1.

Effects of B_2O_3

Exp. No.	Catalyst No.	Catalyst Composition (%) Co + CeO_2 + ThO_2 + B_2O_3 +	Kieselguhr	Reaction Temp. (°C.)	Average Contraction (%)
F_{39}(A–I)	XII_{12}–1	100 15 15 5	100	200	64
F_{41}(A–E)	XII_{12}–1	" " " "	"	"	49
F_{40}(A–G)	XII_{11}–1	" " " 0	"	"	34
F_{45}(A–H)	XII_{16}–1	" " " 10	"	"	49
F_{49}(F)	XII_{16}–1	" " " 10	"	"	42

Table 2.

Effects of B_2O_3 in the Presence of Cu

Exp. No.	Catalyst No.	Catalyst Composition (%) Co + CeO_2 + ThO_2 + B_2O_3 + Cu +	Kieselguhr	Reaction Temp. (°C.)	Average Contraction (%)
F_{48}(A–F)	XII_{19}–1	100 15 15 10 5	100	200	10
F_{43}(A–I)	XII_{14}–1	" 15 15 5 "	"	"	45
F_{47}(A–E)	XII_{18}–1	" 18 18 10 "	"	"	25
F_{44}(A–D)	XII_{15}–1	" 18 18 5 "	"	"	15

Table 3.

Effects of Cu

Exp. No.	Catalyst No.	Catalyst Composition (%) Co + CeO_2 + ThO_2 + B_2O_3 + Cu +	Kieselguhr	Reaction Temp. (°C.)	Average Contraction (%)
F_{48}(A–F)	XII_{19}–1	100 15 15 10 5	100	200	10
F_{45}(A–H)	XII_{16}–1	" " " " 0	"	"	49
F_{47}(A–E)	XII_{18}–1	" 18 18 " 5	"	"	25
F_{46}(A–G)	XII_{17}–1	" " " " 0	"	"	65
F_{43}(A–I)	XII_{14}–1	" 15 15 5 5	"	"	45
F_{39}(A–I)	XII_{12}–I	" " " " 0	"	"	64

(5) Concerning this point, we shall present the results in our subsequent paper to be published elsewhere. (There is some good evidence that the products seem to contain branched chain hydrocarbons.)

Table 4.

Combined Effects of the ThO_2 and CeO_2 Contents

Exp. No.	Catalyst No.	Catalyst Composition (%) Co	CeO_2	ThO_2	B_2O_3	Cu	Kieselguhr	Reaction Temp. (°C.)	Average Contraction (%)
F_{44}(A–D)	XII_{15}–1	100	18	18	5	5	100	200	15
F_{43}(A–I)	XII_{14}–1	"	15	15	"	"	"	"	45
F_{41}(A–E)	XII_{12}–1	"	"	"	"	0	"	"	49
F_{42}(A–I)	XII_{13}–1	"	18	18	"	"	"	"	"
F_{46}(A–G)	XII_{17}–1	"	"	"	10	"	"	"	65
F_{45}(A–H)	XII_{16}–1	"	15	15	"	"	"	"	49
F_{47}(A–E)	XII_{18}–1	"	18	18	"	5	"	"	25
F_{48}(A–F)	XII_{19}–1	"	15	15	"	"	"	"	10

contained no B_2O_3, the activity was estimated as 34%, while in F_{39}(A)–F_{39}(I) series, 64%, and in F_{41}(A)–F_{41}(E), 49%, in both of which the catalyst contained 5% B_2O_3. Furthermore, in F_{45}(A)–F_{45}(H) and F_{49}(F) where the B_2O_3 content amounts to 10%, respectively, the activities have been observed to be 49% and 42%, respectively.

Therefore, we might say that the effect of B_2O_3 on Co+15% CeO_2+15%ThO_2+100% Kieselguhr catalyst is well detectable, as observed in Table 1; but as regards the suitable amount of B_2O_3, since 5% and 10% B_2O_3 give the effects practically to the same extent, it would be better to use a lesser amount of B_2O_3.

While in the presence of Cu, it has been observed that in the series of 18% CeO_2 and ThO_2, 10% B_2O_3 seemed to be better, but in the series of 15% CeO_2 and ThO_2, 5% B_2O_3 appeared to be better.

As regards the effect of Cu[6] on those series, shown in Table 3, regardless of the respective percentage of CeO_2, ThO_2, and B_2O_3, those catalysts without Cu seemed to give much higher activity.

The combined effects of ThO_2 and CeO_2, with or without Cu, in the presence of 10% B_2O_3, 18% series have been observed to be better, while in the presence of 5% B_2O_3, both 15% and 18% series appeared to be practically the same. As to the influence of Cu, here, also the negative effect is definitely shown, as already discussed in connection with Table 3.

Table 5 shows some of the typical results of the influences of pretreatment on the catalyst XII_{16}–1, Co+15% CeO_2+15% ThO_2+10% B_2O_3 +100% Kieselguhr, such as temperature and the duration of heat treatment prior to H_2 reduction and of temperature and the duration of H_2 reduction on the catalytic activity as measured by the average gas contractions.

(6) (a) See also our report V, this Bulletin, **17** (1942), 252.
(b) Fischer, *Brenn-Chem.*, **11** (1930), 489, and the others mentioned in our Report V.
(c) S. Hamai, *J. Chem. Soc. Japan*, "Letter to the Editor" **63** (1942), 88

Table 5.

Effects of Pre-Treatments on the Catalysts

XII_{16}-1, Co+15%CeO_2+15%ThO_2+10%B_2O_3+100%Kieselguhr

Exp. No.	Heat Treatment Prior to H_2 Reduction (°C.)	(hrs.)	H_2 Reduction (°C.)	(hrs.)	Reaction Temp. (°C.)	Average Contraction (%)
F_{45}(A–H)	400	5	375	5	200	49
F_{49}(F)	,,	,,	,,	,,	,,	42
F_{50}(A–J)	,,	,,	300	,,	,,	34
F_{51}(A–F)	,,	,,	400	,,	,,	15
F_{52}(A–H)	,,	,,	350	,,	,,	43
FC_7(A–D)	No heat treatment		,,	10	,,	64

Table 6 demonstrates the contraction percentage as affected by various factors. These results show clearly that whenever we speak of the catalytic activity, every influencing factor must be carefully mentioned, otherwise it is practically meaningless to speak of the catalytic activity.

Table 6.

Contraction percentage as affected by various factors.

Exp. No.	Catalyst No.	Catalyst Composition Co	ThO_2	CeO_2	Kieselguhr	Pre-Treatment: Heat-treatment (°C.)	(hrs.)	Temp. at the Reduction Prior to Heating (°C.)	(hrs.)	React. Temp. (°C)	Ave. Contraction (%)
F_4	I_1-1	100	15	—	100	400	5	350	5	225	40
F_{14}	,,	,,	,,	—	,,	,,	2	,,	,,	,,	25
F_{34}(A–B)	XII_{13}-1	,,	—	15	,,	,,	5	375	,,	200	22
F_{10}	I_4-1	,,	18	—	,,	,,	4	350	,,	225	20
F_5	I_2-1	,,	20	—	,,	,,	2	,,	4	,,	70
F_{17}	,,	,,	,,	—	,,	,,	,,	,,	5	,,	15
F_{18}	,,	,,	,,	—	,,	,,	,,	,,	,,	,,	,,
F_{32}(A–E)	XII_{14}-1	,,	—	20	,,	,,	5	375	,,	200	35
F_6	I_3-1	,,	30	—	,,	,,	,,	350	2	225	70
F_{33}(A–D)	XII_{15}-1	,,	—	30	,,	,,	,,	375	5	200	24
F_{13}	I_6-1	,,	48	—	,,	,,	2	350	,,	225	60
F_{35}(A–D)	XII_8-1	,,	—	48	,,	,,	5	375	,,	200	17
F_9	I_5-1	,,	10	—	,,	,,	2	350	,,	225	6
F_{12}	,,	,,	,,	—	,,	,,	,,	,,	,,	,,	5
F_{31}(A–G)	XII_2-1	,,	—	10	,,	,,	5	,,	,,	200	54

Table 7 summarizes some of the possible correlations among the types of catalysts, their pre-treatments, the gas contraction percentage, oil yields, and gaseous products. As seen in this table, it cannot be so easily generalized that a parallelism between the gas contraction percentage and the oil yield, as evidenced by F_{49}(F), where the oil yield amounts to 171.7 c.c./m.^{3} with 42% contraction, while F_{39}(A–I) gives 121 c.c./m.^{3} with 64% contraction; F_{45}(A–H), 124.4 c.c./m.^{3} with 49% contraction, F_{46}(A–G), 127.1 c.c./m.^{3} with 65% contraction; and FC_7 (A–D), 129.4 c.c./m.^{3} with 64% contraction, respectively, although it

Table 7.

Exp. No.	Catalyst No.	Catalyst Composition (%)						Pre-treatment				Ave. Contraction (%)	Gaseous Products			O.I-yield cc/M³	Space Velocity
		Co+CeO_2+ThO_2+B_2O_3+Kieselguhr					+Cu	Heat-treat. (°C.)	(hrs.)	H_2 Reduction (°C.)	(hrs.)		CH_4 (%)	C_2H_6 (%)	Olefins (%)		
F_{39}(A–I)	XII_{12}–1	100	15	15	5	100	—	400	5	375	5	64	10	0.9	1.2	121	330
F_{40}(A–I)	XII_{11}–1	"	"	"	—	"	—	"	"	"	"	34	0	0	0.5	75	280
F_{41}(A–E)	XII_{12}–1	"	"	"	5	"	—	"	"	"	"	49	"	"	0.7	78	330
F_{42}(A–I)	XII_{13}–1	"	18	18	"	"	—	"	"	"	"	"	3.9	"	1.5	98	231
F_{43}(A–I)	XII_{14}–1	"	15	15	"	"	5	"	"	"	"	45	5.5	"	0.2	93.2	233
F_{44}(A–D)	XII_{15}–1	"	18	18	"	"	"	"	"	"	"	15	0	"	0.4	21.7	239
F_{45}(A–H)	XII_{16}–1	"	15	15	10	"	—	"	"	"	"	49	11.5	"	0.5	124.4	244
F_{46}(A–G)	XII_{17}–1	"	18	18	"	"	—	"	"	"	"	65	6.7	1.2	1.7	127.1	220
F_{47}(A–E)	XII_{18}–1	"	"	"	"	"	5	"	"	"	"	25	0	0	0.3	67.2	237
F_{48}(A–F)	XII_{19}–1	"	15	15	"	"	"	"	"	"	"	10	"	"	0.2	26.5	242
F_{49}(F)	XII_{16}–1	"	"	"	"	"	—	"	"	"	"	42	"	"	0.0	171.7	248
F_{50}(A–F)	"	"	"	"	"	"	—	"	"	300	"	34	—	—	—	95.1	246
F_{51}(A–F)	"	"	"	"	"	"	—	"	"	400	"	15	0	0	0.5	51.9	239
F_{52}(A–H)	"	"	"	"	"	"	—	"	"	350	"	43	3	2.4	0.7	63.1	242
FC_7(A–D)	"	"	"	"	"	"	—	—	—	"	10	64	16.2	1.1	1.6	129.4	"

(*) CH_4 formation tends to zero as time proceeds.

might be said that 50–65% gas contraction usually gives 120–130 c.c./m.^{3} in these series of catalysts.

Thus far we have tabulated some of the typical results of the investigations concerning the effects of promoters on the Co type catalyst, with respect to the gas contraction percentage as a measure of the catalytic activity, also with regard to the oil yield as well; and also we pointed out that the fundamental difficulty as to get a general statement concerning the gas contraction percentage as related to the oil yield—which is so far simply considered as somewhat parallel—but actually it is not so simple as expected. Some authors have just considered these problems as the simplest case, i.e., a parallelism exists between the gas contraction and the oil yield, regardless of the amount of gaseous products formed, such as CH_4, C_2H_6 or C_2H_4. It is quite evident that, whenever CH_4 formation predominates, the contraction percentage is enormously high and the oil yield is not so appreciable—usually, when CH_4 formation is very much appreciable, the oil yield is negligibly small, as we often pointed out[5] previously. Concerning suitable conditions for the synthesis of liquid hydrocarbons, it may probably be stated that the catalyst must be so rearranged that CH_4 formation is so restricted, or inhibited, as to direct the reaction of the liquid hydrocarbon synthesis on the catalytic surface, as required by our mechanism[7], previously discussed.

Summary.

(1) The effects on the Co type catalyst of such promoters as B_2O_3 and Cu, and the combined effects of ThO_2 and CeO_2 on the catalytic activity have been investigated and discussed.

(2) The effects of the pre-treatment on the catalytic activity have been investigated and discussed.

(3) It has been shown that there is a fundamental difficulty to generalize a parallel relationship between the gas contraction and the oil yields.

(4) In discussing the catalytic activity, that the CH_4 formation must be carefully segregated whenever we speak of the catalytic activity as to its oil forming ability has been pointed out as of paramount importance.

In conclusion, the author takes this occasion to express his sincere thanks to Dr. T. Marusawa, Former Director of the Institute and Dr. M. Sato, Director of the Institute, for their interests and encouragement during these series of investigations and also for the permission of the publication; also he thanks to colleagues for their cooperation and to Messrs. Hayashi, Shimamura, Kuwabara, Igarashi and Fujiwara who have been willing to assist him in the experimental part of this investigation.

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(7) Report II, this Bulletin, **16** (1941), 213.

Hydrocarbons from Carbide (A) IV. Non-Catalytic Polymerization under Ordinary Pressure. Acetylene-Carbide System and General Remarks.

By Ryoji NEGISHI and Osamu KAMIIKE.

(Received February 10, 1942.)

This paper will conclude our investigations on the non-catalytic direct synthesis of hydrocarbon liquid products from calcium carbide under ordinary pressure. The paper consists of two parts: the first part deals with the studies on acetylene-carbide system and the second gives a supplementary discussion and, at the same time, a resumé of the results of the entire series of investigations, consisting of the following systems:

Hydrogen—carbide,
Carbon dioxide—carbide,
Carbon monoxide (and water gas)—carbide,
Hydrogen chloride—carbide, and
Acetylene—carbide.

With the accumulation of the results with various gases, we feel more confident that we are now in a better position to picture the true affairs of the polymerization of nascent acetylene molecules, even in a system where the carrier gas itself may undergo polymerization. In fact, we have hoped that the total liquid yield may be increased by the polymerization of the very gas introduced, and for this reason, we have attempted to study the effects of acetylene and its mixtures with hydrogen or carbon dioxide. We have further hoped that by the introduction of acetylene, the formation of free acetylene from the carbide may be prevented, or suppressed, and thereby the nascent acetylene may be made more available for liquid synthesis.

In this paper we have made most of the runs at 340°C., which seems to be the most satisfactory temperature, and one run at 420°C. to make more clear the real effect of the carrier gas on the total yield of liquid products. Preparation of acetylene and experimental method have been already given in Paper (A) II[1].

Results and Discussion. Results are given in Table 11.* The first question that may be raised is whether the introduction of acetylene suppresses the formation of free acetylene from the carbide or not. Our data given in Table 12, seem to indicate it positively. In the table the results of only those experiments have been considered** in which except for

(1) R. Negishi and O. Kamiike, this Bulletin, **17** (1942), 118; also R. Negishi and O. Kamiike, *J. Soc. Chem. Ind.*, Japan. **45** (1942), 135.

* Numbering of the Tables and Figures is consecutive from (A) II to the final paper.

** Percentage of free C_2H_2 varied from 20.3 to 36.1 for all the other runs at 340°C. involving mixtures of gases.

Table 11. Acetylene Systems.

Experimental No.	I_L 70	I_L 75	I_L 68	I_L 71	II_L 22
Reaction Temp. (°C.)	340	340	340	340	420
Gas	C_2H_2	$C_2H_2+H_2$	$C_2H_2+CO_2$	$C_2H_2+CO_2$	C_2H_2
Saturation Temp. (°C.)	79.7	79.8	78.8	79.8	65.5
Ratio Gas to Water (Partial Press.)	$C_2H_2:H_2O$ 1:0.86	$C_2H_2:H_2:H_2O$ 1 : 1 : 2.67	$C_2H_2:CO_2:H_2O$ 1 : 3 : 4	$C_2H_2:CO_2:H_2O$ 1 : 3 : 4	$C_2H_2:H_2O$ 2.7 : 1
Time of Contact (sec.)	25.9	28.9	18.3	22.9	23.7
Liquid Products (g.)	22.4	17.5	22.9	18.8	8.3
Water (g.)	1.5	0.7	7.2	3.8	1.0
Oil % on Reacted Carbide Carbon	40.6	34.5	36.9	30.0	130
Oil (total Wt.) % on Reacted Carbide C_2H_2	47.2	38.0	40.7	33.6	137
Carbon Balance	102.3	96.0	95.8	104.5	99.0
Weight Balance	102.2	98.8	100.4	99.5	99.3

Table 12.

Exp. No.	I_L 34	I_L 35	I_L 44	I_L 57	I_L 65	I_L 70	I_L 68	I_L 71	I_L 75
Gas	H_2	N_2	CO	CO_2	CO_2+HCl	C_2H_2	$C_2H_2+CO_2$	$C_2H_2+CO_2$	$C_2H_2+H_2$
Free C_2H_2 (%)	+36.1	+26.7	+34.3	+27.8	+28.3	−8.4	+16.6	−42.2	−15.7

acetylene and HCl systems pure gases are used. The plus sign means that free acetylene has been formed while the minus means that the introduced acetylene has reacted; in other word, it is equivalent of saying that there is no formation of free acetylene. Minus 42.2% is definitely too high, and plus 16.6 is difficult to explain.*

Another question that may arise is whether or not the total liquid yield, based on the reacted carbide acetylene (and carbon), increases in these systems. The answer is again positive but with certain reservations. The results of Table 11 indicate that the effect of acetylene on the total yield is striking only when its concentration is relatively high, as for example, I_L–70 and II_L–22. When acetylene is diluted with an inert gas, such as H_2 or CO_2, and its concentration becomes relatively low, its effect on the total liquid yield disappears, as shown by I_L–75, I_L–68, and I_L–71. However, the presence of acetylene, even in a small concentration, has a striking effect on the suppression of the formation of free aceytlene, as has been mentioned in the preceding paragraph. These effects, coupled with the fact that some of the introduced acetylene is actually used up, suggest that the role of the introduced acetylene is to form principally gaseous products, which in the absence of the acetylene are formed at the expense

* It may be added here that the results of I_L–68 are less reliable.

of the carbide, or that of the nascent acetylene molecules. It is interesting that the liquid yield at 420°C. is much larger than at 340°C., quite contrary to the results of the other systems, although the effect of the acetylene concentration cannot be entirely dismissed. Nevertheless, this point is in accord with the fact that the liquid formation by non-catalytic acetylene polymerization becomes appreciable only above 400°C. and optimum in the range, 500 to 700°C.[2]

The effect on the liquid yield of a diluent gas is small, and the final yield is mainly determined by the concentration of the water vapor. It may be added, however, that there exists an optimum concentration of the water vapor. A ratio not differing too far from 0.8 to 1.0 seems most favorable under our experimental conditions.

The results of elementary analysis are given in Table 13. The results of gas analysis are given in Table 14, and here, again, they should be considered, as in a previous paper[3], qualitatively rather than quantitatively. In spite of the fact that some of the hydrogen used in effecting desorption

Table 13. Elementary Analysis.

Exp. No.	I_L 68		I_L 70		I_L 71		I_L 75		II_L 22	
	Trap.	Cond.	Trap.	Cond.	Trap.	Cond.	Trap.	Cond.	Trap.	Cond.
Element C....	74.98	84.69	67.98	86.27	79.76	82.66	79.69	86.72	74.10	81.96
" H....	9.37	8.62	10.21	8.73	9.97	8.61	9.01	9.26	10.30	8.19
" O....	15.65	6.69	21.81	5.00	10.27	8.73	11.20	4.01	15.60	9.85

Table 14. Gas Analysis (Average values).

Exp. No.	I_L 68	I_L 70		I_L 71			I_L 75		II_L 22	
Gas		Reacted	Desorp.	Reacted	Desorp.	Orig.	Reacted	Orig.	Reacted	Orig.
CO_2	38.2	2.4	0.6	36.5	4.0	74.3	1.0	0.8	1.6	6.9
C_2H_2	34.4	79.2	22.1	47.7	14.1	24.7	30.8	45.5	75.4	92.9
C_2H_4	0.1	0.2	0.6	0.2	0.4	—	0.6	0.0	0.5	—
C_nH_{2n}	0.2	0.6	1.1	0.4	0.7	—	0.8	0.0	0.9	—
O_2	0.7	0.6	0.6	0.6	0.5	—	0.8	1.0	0.5	—
CO	0.3	0.3	0.4	0.3	0.3	—	0.3	0.0	0.3	—
H_2	21.3	9.6	62.3	8.8	70.3	—	57.4	47.9	12.4	—
CH_4	1.7	4.0	8.7	1.7	7.0	—	4.1	0.4	6.1	—
N_2	2.0	3.3	3.1	3.8	3.0	1.0	3.7	4.2	1.0	0.2

is mixed in the effluent reacted gas, the hydrogen contents in runs I_L–70 and I_L–71, which are at 340°C., are lower than that of II_L–22, which is at 420°C. and in which no desorption has been effected. A similar situation exists for the methane contents of these runs, and these facts are consonant with the effect ascribable to the difference in the reaction temperatures.

(2) G. Egloff, "The Reactions of Pure Hydrocarbons," Reinhold Publishing Corp., N.Y., (1937); C. Ellis, "The Chemistry of Petroleum Derivatives," Reinhold Publishing Corp., N.Y., Vols. I and II, (1934 and 1937).

(3) R. Negishi and O. Kamiike, this Bulletin **17** (1942), 244.

When the contents of methane in the effluent gas of desorption in I_L–70 and I_L–71 are considered, it is evident that they are higher than those in the respective effluent gases during the normal course of reaction. The difference must be real. When the temperature is increased to effect desorption, quite an appreciable amount of water is always condensed out along with the liquid products, even when a dry gas is used. The source of this water is not clear, but that is of no consequence in our present discussion. What appears significant is that this water reacting with the carbide, produces acetylene which probably is then transformed into methane more effectively at higher temperature. As has been mentioned before[3], the effect of desorption is apparent only in I_L–71 in which carbon dioxide is present.

This system will conclude the experimental work on the non-catalytic direct synthesis of hydrocarbons from calcium carbide under ordinary pressure, and in the next section of this paper, we shall treat the subject from a broader perspective to give more coherence to the isolated facts obtained in the individual systems so far investigated.

Concluding Remarks. As we have already seen, hydrogen and nitrogen are without effect[1]; carbon dioxide has a pronounced beneficial effect[3] while carbon monoxide has rather harmful ones[3]; acetylene increases the total yield owing to the circumstance that it itself polymerizes under certain conditions; and, finally, hydrogen chloride has shown to give somewhat harmful effects only when its concentration is high[3]. We have also seen that desorption shows effects only when CO_2 (and its mixtures) is used as a carrier gas. Although these gases have varied in their effects on the total liquid products, they are without appreciable influence on the character of the products. This point has been briefly mentioned elsewhere[3], but it becomes quite plausible in the light of the more complete set of data, which are shown in Table 15.

As can be readily seen from Table 15, the oxygen contents of the condensates in the condenser and in the trap differ widely, as is also the case with their H/C ratios. When the average ratios of H/C, 0.1309 and 0.1028, for the liquid in the trap and the condenser, respectively, are compared, there will be a difference of 27% between them, provided no correction for the oxygen content is taken into account; when corrected, the corresponding values are 0.0959 and 0.0890, and the difference is about 8% which is a notable reduction from that of the uncorrected. Moreover, the individual ratios for the corrected values differ from the average less markedly. This is interesting, because it gives some support to the validity of our assumptions that the oxygen is principally alocoholic and that the gases used are without influence on the character of the products.

The results of elementary analysis of the condenser condensates* also give good supporting evidence for the independence of nascent acetylene

* The results of the trap are not so uniform as those of the condenser, but this is due to the fact that the amount of the condensates in the former is very much smaller (at times, less than 10% of the condenser, or about 1 c.c.), and the results of analysis are less accurate. There is another probable source of error, which is more pronounced in the trap than in the condenser. It is the amount of water which may have dissolved in the respective condensates. A larger H/C ratio of trap as compared with that of condenser is suggestive.

Table 15.

Exp. No.	Gas Used	Elementary Analysis	Trap	Cond.	H/C Ratio Found Trap	H/C Ratio Found Cond.	H/C Ratio Correct. for MeOH Oxygen Trap	H/C Ratio Correct. for MeOH Oxygen Cond.	On Reacted Carbide Carbon (%) Methane C in Reacted Gas	On Reacted Carbide Carbon (%) Decomp.+Poly. Carbon in Residue
		C	74.79	86.57						
I_L35*	N_2	H	9.96	8.61	0.1295	0.099	0.100	0.0894	3.5	20.7
		O	13.25	4.82						
		C	75.36	85.99						
I_L34	H_2	H	10.22	8.39	0.1355	0.0975	0.1024	0.0862	6.1	18.8
		O	14.40	5.62						
		C	74.98	83.19						
I_L57	CO_2	H	9.37	8.76	0.1250	0.1053	0.0853	0.0864	3.9	23.1
		O	15.65	8.05						
		C	83.02	84.02						
I_L41	CO_2+H_2	H	10.10	8.47	0.1214	0.1000	0.1070	0.0841	2.3	24.5
		O	6.88	7.52						
		C	82.02	84.60						
I_L44	CO	H	9.71	8.69	0.1182	0.1027	0.1008	0.0881	7.3	48.9
		O	8.27	6.71						
		C		85.20						
I_L50	$CO+H_2$	H	Combined	8.76	Combined	0.1025	Combined	0.0898	3.4	43.1
		O		6.04						
		C	74.29	79.79						
I_L64	HCl, $3.5+CO_2$	H	10.10	8.78	0.1360	0.1100	0.0989	0.0833	3.5	23.4
		O	15.61	11.43						
		C	67.70	84.96						
I_L65	HCl, Dil.$+CO_2$	H	10.48	8.85	0.1550	0.1042	0.1020	0.0957	2.3	28.3
		O	21.82	6.19						
		C	67.98	86.27						
I_L70	C_2H_2	H	10.21	8.73	0.1500	0.1015	0.0923	0.0906	12.5	44.63
		O	21.81	5.00						
		C	79.69	86.72						
I_L75	C_2H_2 $+H_2$	H	9.01	9.26	0.1130	0.1070	0.0871	0.0937	6.4	41.50
		O	11.20	4.01						
		C	74.98	84.69						
I_L68	C_2H_2 $+CO_2$	H	9.37	8.62	0.1250	0.1015	0.0862	0.0873	3.8	28.4
		O	15.65	6.69						
		Average			0.1309	0.1029	0.0959	0.0890		

* Least reliable.

polymerization, which we shall henceforth refer to as the specificity of nascent acetylene polymerization. As evident from Table 15, the results are quite similar in every case except for those of I_L–64. The fact that a ratio of H/C is near that of C_2H_2 but always larger is probably real and significant. The meaning of this is, among others, first, the mechanism of the main reaction of the nascent acetylene molecules may be written as

$$n(C_2H_2) \rightleftharpoons (C_2H_2)_n,$$

second, there is a slight amount of hydrogenation of the products, even in the absence of any catalyst. This is what we have anticipated in one of our papers[4] At the instance the carbide reacts with water, there may exist some rather reactive hydrogen molecules or atoms, some of which may take part in hydrogenation[5]. The ratio of the average value of H/C to that of acetylene gives a measure of the degree of hydrogenation; it is 1.07, or about 7% is hydrogenated.

We cannot draw a conclusion as to the mechanism of the main reaction merely from the circumstance alone that the ratio of H/C is near that of acetylene, since it is quite possible that the average value of elementary analysis of the numerous components* contained in the products may be that of acetylene as far as its H/C ratio is concerned. However, it may be carried to the conclusion by a combination of the following evidences. Properly controlled low-temperature polymerization of acetylene[7] will convert it into monovinylacetylene; a dimer, divinylacetylene; a trimmer[8]; and a tetramer[9][5]. Spark, Rosen, and Frolich in their interesting paper[10], "Dimerization of Petroleum Hydrocarbons," have assumed that complicated hydrocarbons can be built up by a series of dimerizations involving the well-known 1, 3 rearrangement of hydrogen and have applied this principle to acetylene. According to them a dimer, vinylacetylene, is formed which may undergo either to vinyldivinylacetylene, CH_2–CH–C≡C–CH=CH–CH=CH_2, or to styrene by ring closure. Styrene has been identified[6][11]. Recently, butadiene has been

(4) R. Negishi, O. Kimura, and O. Kamiike, *Rev. Phys. Chem., Japan*, **15** (1941), 31.

(5) H. A. Taylor and A. Van Hook. *J. Phys. Chem.*, **39** (1935), 811. They have concluded from their homogeneous thermal polymerization of acetylene and its hydrogenation in the temperature range 495 to 535°C. that the principal processes (polymerization and hydrogenation) are interpreted as bimolecular with energies of activation of 40,500 and 42,000 calories, respectively. The efficiency of the association is high, but in the presence of excess of hydrogen, the hydrogenation process becomes predominant.

* Indicated by the absence of sharp breaks in the distillation curve and by the large number of the products, as shown in Table 16, identified by Schlapher and Stadler[6] in their analysis of the cuprene-tar, the liquid products obtained during the formation of cuprene.

(6) Schlapher and Stadler, *Helv. Chim. Acta*, **9** (1926), 185.

(7) C. Ellis, Ref. 2, Vol. II, p. 701 ff. (1937).

(8) Acetylenebivinyl, CH_2=CHCH=CHC≡CH, another trimer of acetylene has been obtained by A. K. Klebanskii, U. A. Dranitzina, and I. M. Dobromilskaya, Compt. rend. acad. sci., (URSS), **2** (1935), 229.

(9) Pease, *J. Am. Chem. Soc.*, **51** (1929), 3470. He concludes that the rate determining process is the primary reaction involving two molecules of acetylene, and the major reaction involves four molecules of acetylene giving a tetramer. Taylor and Van Hook (*loc. cit.*) assume that the main reactions of acetylene in the presence of hydrogen are

$$4C_2H_2 = (C_2H_2)_4 \quad \text{and}$$

$$C_2H_2 + H_2 = C_2H_4.$$

(10) W. J. Spark, R. Rosen, and P. K. Frolich, *Trans. Faraday Soc.*, **35** (1939), 1040.

(11) M. E. Cupery and W. H. Carothers, *J. Am. Chem. Soc.*, **56** (1934), 1625.

prepared directly from acetylene[12]. In the light of the foregoing evidences, it is not unreasonable to assume that the main mechanism of the nascent acetylene polymerization is as written above; moreover, it becomes probable that some sort of chain-compounds are formed first which are then transformed into aromatic and condensed hydrocarbons[13]. In connection with this transformation, a recent paper by Thomas, Egloff, and Morrell[14] is highly suggestive.

We shall say a word concerning the beneficial effect of carbon dioxide in passing. It is difficult to point out definitely what the effect is but we believe that it is associated, to no small extent, with the destruction

Table 16. Physical Constants of Cuprene-Tar.

Compound	Formula	d^{20}	Boiling Pt. °C at 760 mm.	Mol. Wt.	H/C
Hexenes	C_6H_{12}	0.681–0.6938	64.1–68.1	84	0.167
Octene	C_8H_{16}	0.7155	123	112	0.167
Benzene	C_6H_6	0.8707	80.08	78	0.0833
Toluene	C_7H_8	0.8658	110.5	92	0.0952
Xylenes	C_8H_{10}	0.8612–0.8745	138.4–144.4	106	0.1041
Ethylbenzene	C_8H_{10}	0.8669	136.1	106	0.1041
Styrene	C_8H_8	0.9074	146	104	0.0833
Methylstyrene	C_9H_{10}	—	—	118	0.0927
Trimethylbenzenes	C_9H_{12}	0.8634–0.895	164.64–176.1	120	0.1112
Ethylmethylzenzenes	C_9H_{12}	0.862–0.873	162–162.5	120	0.1112
Propylbenzenes	C_9H_{12}	0.862–0.864	152–159.45	120	0.1112
Naphthalene	$C_{10}H_8$	1.145	217.9	128	0.0666
Methylnaphthalenes	$C_{11}H_{10}$	1.052–1.029	242–245	142	0.0758
Ethylnaphthalene	$C_{12}H_{12}$	1.059	258 (decomp)	156	0.0833
Dimethylnaphthalenes	$C_{12}H_{12}$	1.001–1.008	261–266	156	0.0833
Anthracene	$C_{14}H_{10}$	1.025	354–5	178	0.0596
Hexahydronaphthalene	$C_{10}H_{14}$	0.934			
Butylbenzenes		0.862–0.8673	168.7–180		
Cymenes		0.8510–0.876	175–177		
Propyltoluenes		0.864	176–184	134	0.1166
Diethylbenzenes		0.860–0.865	182–184.5		
Dimethylethylbenzenes		0.861–0.877	185–189		
Tetramethylbenzenes		0.880–0.901	195–204		

of $Ca(OH)_2$ (and CaO). According to Berl and Hofmann[15], CaO is unfavorable to acetylene polymerization and turns the reaction toward the formation of methane, hydrogen, and carbon. When our results in

(12) A. A. Balandin, Ya. T. Eidus, and E. M. Terent'eva, *Compt. rend. acad. sci.*, (URSS), **27** (1940), 343.

(13) E. Bergman, *Trans. Faraday Soc.*, **35** (1939), 1025; G. B. Kistiakowsky and W. W. Ransom, *J. Chem. Phys.*, **7** (1939), 725.

(14) C. L. Thomas, G. Egloff, and J. C. Morrel, *Chem. Rev.*, **28** (1941), 1. This interesting paper summarizes the reactions of hydrocarbons in electrical discharges, but the mechanism of acetylene polymedization in general is also included.

(15) E. Berl and K. W. Hofmann, *Z. angew. Chem.*, **44** (1931), 259.

Table 15 are examined, whenever CO_2 is used, a ratio of methane carbon, as well as that of free carbon, to carbide carbon is smaller.*

Hydrogen chloride seems without appreciable effect, and this is probably due to the fact that it may not react with CaO but slightly. In I_L–62 (Table 6[3]), where the average concentration of the acid is 26% by weight, the carbonate carbon in the residue is 10.4% while that in the hydrogen system[1] is from 3.7 to 12.9%; in I_L–75 (Table 11) in which a mixture of acetylene and hydrogen is used, it is 8%. Since HCl seems without effect on the carbonate, it may neither have any effect on CaO**.

The facts that the presence of the carbide increases the magnitude of $-\Delta F$[4] and that the nascent acetylene molecules possess high reactivity might lead to a conclusion that there would be an improvement in the yield of hydrocarbon liquids. The answer to this point is hinted at when the results of I_L–57 (Table 3[3]) are compared with those obtained by Shiomi and Iwamoto[16] and Amemiya[17], as shown in Table 17. As can be seen from Table 17, under the respective optimum conditions the polymerization of nascent acetylene gives, even in the absence of catalyst, the highest yield both in volume and weight. The fact that the lower the reaction temperature, the lighter are the products is probably due to the predominance of catalytic effect over that of $-\Delta F$, or the chemical tendency, which favors the formation of heavier products in the carbide reactions[4].

Table 17. Comparison between Polymerizations of Ordinary and Nascent Acetylene.

Experimenter	Catalyst	Temp. (°C.)	Max. Yield		Approx. Density
			c.c./cbm.	gr./cbm.	
Shiomi and Iwamoto ..	Co:Ni:Cr_2O_3 Acid clay	208	405	320	0.778*
Amemiya	Fe:Ni Kieselguhr	290	455.6**	389	0.855
Negishi and Kamiike..	None	340	486	460	0.9–1.0

* For the fraction boiling between 170 and 200°C.

** The more recent result by him is (ref. 17b), under the following conditions: Catalyst Fe:Ni:Co:Kieselguhr (90:5:5:1000)+2% K_2CO_3, 3 g. as metal; reaction gas C_2H_2:H_2=1:4; flow rate 200 c.c./min.; reaction Temp.°C. (270?), 478.5 c.c./cbm.

In Shiomi and Iwamoto's experiment, given in Tables 18 and 19, it is obvious that the fraction boiling up to 300°C. is about twice as large and the densities of various fractions are much less than ours. In their investigations they have obtained only 26.9% aromatic; similarly, Amemiya has obtained about 23%* aromatic for the fractions boiling up to 350°C. In ours, on the other hand, we are quite reasonable in assuming,

* High polymers and free carbon are determined together, and there is some uncertainty in the values of the individual components.

** Since the results of I_L–62 are least reliable, this argument must be taken with certain reservations.

(16) Shiomi and Iwamoto, *J. Soc. Chem. Ind., Japan*, **41** (1938), 831.

(17) T. Amemiya, *ibid.*, **42** (1939), 692; (b) *J. Fuel Soc., Japan*, **21** (1941), a45.

*** Calculated from his data given in Ref. 17b, pp. a56 and a57.

Table 18. Results of Distillation.

Negishi and Kamiike			Shiomi and Iwamoto	
Distillation Range Temp. (°C.)	Vol. (%)	Density at 25°C.	Range of Distillation	Fraction Vol. (%)
<100	1.8	—	—	—
100–150	5.7	0.837*	<150	28.7
150–200	7.8	0.9084	150–200	15.5
200–250	22.3	0.957	200–270	23.6
250–300	10.1	0.971	270–300	11.5
300–326	25.4	—	Above 300	19.6
Residue.....	22.1 (Wt. %)			

* For fraction below 150°C.

Table 19. Density of Products.

Temp. Range (°C.)	<110	110–140	140–170	Above 170	Experimenter
Density$_4^{20}$	0.685	0.739	0 749	0.778	Shiomi and Iwamoto
Temp. Range	Below 150		150–200		Negishi and Kamiike
Desnty at 25°C.	0.837		0.9084		

judging from the boiling ranges and densities, that the major fraction of the products is aromatic. This assumption becomes more plausible in the light of the identification made by Schlapher and Stadler[6] of the cuprenetar (Table 16). The physical constants of the substances identified, as well as some of the unidentified substance having the empirical formula, $C_{10}H_{14}$, in the Table have been taken from the Science of Petroleum[18].

Finally, we may say that many of our observations in this series of investigations are without adequate interpretation; to mention a few, the real effects on the liquid yield of carbon monoxide, hydrogen chloride, and desorption and the real nature of the individual components in the product. The role of a catalyst must be made clear in near future, but at this stage of progress, we may say with some confidence that in these reactions involving the carbide, it is not the question of the activation of the reactants, but of the selectivity, or the specificity, of the catalyst that is most pertinent.

Summary.

It has been shown that when acetylene is used as a carrier gas, the percentage of the total liquid products, based on the reacted carbide acetylene (or carbon), increases owing to the polymerization of the carrier gas itself, provided its concentration is sufficiently high. If the concentration is low, the effect of the introduced acetylene appears limited merely to the suppression of the formation of free acetylene.

(18) The Science of Petroleum, Vol. 11 (1928), Oxford Press.

An explanation for a higher content than in the reacted gas of methane in the effluent gas used for desorption has been given for the acetylene system.

The supplementary data in support and evidence for the reasonableness of the over-all mechanism of nascent acetylene polymerization, which may be written

$$n(C_2H_2) = (C_2H_2)_n,$$

have been given.

It has been indicated that the efficacy of the synthesis of hydrocarbon liquids directly from calcium carbide is higher than even the catalytic polymerization, so far reported in literature, of ordinary acetylene.

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